

# Urban Emissions of Water Vapor in Winter

**Olivia E. Salmon<sup>1</sup>, Paul B. Shepson<sup>1,2</sup>, Xinrong Ren<sup>3,4</sup>, Allison B. Marquardt Collow<sup>5,6</sup>, Mark A. Miller<sup>7</sup>, Annmarie G. Carlton<sup>8</sup>, Maria O. L. Cambaliza<sup>1,9</sup>, Alexie Heimburger<sup>1</sup>, Kristan L. Morgan<sup>2</sup>, Jose D. Fuentes<sup>10</sup>, Brian H. Stirm<sup>11</sup>, Robert Grundman II<sup>11</sup>, Russell R. Dickerson<sup>4</sup>**

<sup>1</sup>Department of Chemistry, Purdue University, West Lafayette, Indiana, USA, <sup>2</sup>Department of Earth, Atmospheric, and Planetary Sciences and Purdue Climate Change Research Center, Purdue University, West Lafayette, Indiana, USA, <sup>3</sup>Air Resources Laboratory, National Oceanic and Atmospheric Administration, College Park, Maryland, USA, <sup>4</sup>Department of Atmospheric and Oceanic Science, University of Maryland, College Park, Maryland, USA, <sup>5</sup>Universities Space Research Association, Columbia, Maryland, USA, <sup>6</sup>NASA/GSFC Code 610.1, Global Modeling and Assimilation Office, Greenbelt, Maryland, USA, <sup>7</sup>Department of Environmental Sciences, Rutgers University, New Brunswick, New Jersey, USA, <sup>8</sup>Department of Chemistry, University of California, Irvine, California, USA, <sup>9</sup>Now at the Department of Physics, Ateneo de Manila University, Quezon City, Philippines, <sup>10</sup>Department of Meteorology, The Pennsylvania State University, University Park, Pennsylvania, USA, <sup>11</sup>School of Aviation and Transportation Technology, Purdue University, West Lafayette, Indiana, USA

Corresponding author: Olivia E. Salmon ([osalmon@purdue.edu](mailto:osalmon@purdue.edu))

## Key Points:

- Unique airborne data reveals elevated H<sub>2</sub>O<sub>v</sub> mole fractions downwind of urban areas in winter months
- Estimates of H<sub>2</sub>O<sub>v</sub> emitted from fossil fuel combustion account for less than 10% of the observed H<sub>2</sub>O<sub>v</sub> enhancement in the urban outflow
- Combustion and evaporative cooling cannot account for the urban H<sub>2</sub>O<sub>v</sub> excess, leaving enhanced urban evaporation as a plausible explanation

## Abstract

Elevated water vapor ( $\text{H}_2\text{O}_v$ ) mole fractions were occasionally observed downwind of Indianapolis, IN, and the Washington, D.C.-Baltimore, MD, area during airborne mass balance experiments conducted during winter months between 2012 and 2015. On days when an urban  $\text{H}_2\text{O}_v$  excess signal was observed,  $\text{H}_2\text{O}_v$  emissions estimates range between  $1.6 \times 10^4$  and  $1.7 \times 10^5 \text{ kg s}^{-1}$ , and account for up to 8.4% of the total (background + urban excess) advected flow of atmospheric boundary layer  $\text{H}_2\text{O}_v$  from the urban study sites. Estimates of  $\text{H}_2\text{O}_v$  emissions from combustion sources and electricity generation facility cooling towers are 1-2 orders of magnitude smaller than the urban  $\text{H}_2\text{O}_v$  emission rates estimated from observations. Instances of urban  $\text{H}_2\text{O}_v$  enhancement could be a result of differences in snowmelt and evaporation rates within the urban area, due in part to larger wintertime anthropogenic heat flux and land cover differences, relative to surrounding rural areas. More study is needed to understand why the urban  $\text{H}_2\text{O}_v$  excess signal is observed on some days, and not others. Radiative transfer modeling indicates that the observed urban enhancements in  $\text{H}_2\text{O}_v$  and other greenhouse gas mole fractions contribute only  $0.1^\circ\text{C day}^{-1}$  to the urban heat island at the surface. This integrated warming through the boundary layer is offset by longwave cooling by  $\text{H}_2\text{O}_v$  at the top of the boundary layer. While the radiative impacts of urban  $\text{H}_2\text{O}_v$  emissions do not meaningfully influence urban heat island intensity, urban  $\text{H}_2\text{O}_v$  emissions may have the potential to alter downwind aerosol and cloud properties.

## 1. Introduction

Gradients in humidity between urban and rural environments have been observed for decades, with cities found to be both drier and more humid than surrounding rural areas depending on time of day or year [Kuttler *et al.*, 2007; Liu *et al.*, 2009; Hall *et al.*, 2016]. In general, cities are expected to be drier during the day than surrounding rural areas [Arnfield, 2003]. Soil and vegetation retain moisture and are capable of larger rates of evapotranspiration, in contrast to impervious urban surfaces like asphalt and concrete. Instances when urban atmospheric moisture levels are in excess of rural areas, referred to as urban moisture excess (UME), are often observed at night when urban heat islands (UHIs) are at their strongest, if dew point temperatures are reached in the surrounding rural area but not the city [Hage, 1975; Bornstein and Tam, 1977; Holmer and Eliasson, 1999; Deosthali, 2000; Kuttler *et al.*, 2007]. Additionally, UME events have been observed during the daytime in mid-latitude cities during winter months [Hage, 1975; Ackerman, 1987], and in some cities throughout the year [Kuttler *et al.*, 2007; Hall *et al.*, 2016].

These gradients are frequently rooted in differences between urban and rural energy balance and moisture sources [Arnfield, 2003]. Faster rates of snowmelt and local advection-assisted evapotranspiration have been reported in urban areas [Oke, 1979; Oke and McCaughey, 1983; Oke *et al.*, 1992; Bengtsson and Westerström, 1992; Neumann and Marsh, 1998; Moriwaki and Kanda, 2004]. Energy flux partitioning in urban areas is sensitive to the Bowen ratio (ratio of sensible to latent heat flux), which is low following precipitation events [Offerle *et al.*, 2006; Ward *et al.*, 2013; Ramamurthy *et al.*, 2014; Ao *et al.*, 2016]. Urban latent heat fluxes during the winter-spring transition can respond strongly to soil moisture thaw and snowmelt [Offerle *et al.*, 2006; Lemonsu *et al.*, 2008; Leroyer *et al.*, 2010]. However, suburban and urban areas within the same city can exhibit different relationships between latent heat flux and the physical state and availability of moisture on and within impervious and vegetated land cover [Bergeron and Strachan, 2012]. Direct anthropogenic emissions of heat and moisture from combustion sources, industry, and home heating and cooling have been reported to be significant [Hage, 1972; Grimmond, 1992; Moriwaki *et al.*, 2008; Sailor, 2011; Gorski *et al.*, 2015], and have also been implicated as contributors to UME [Hage, 1972, 1975; Bornstein and Tam, 1977; Ackerman, 1987]. Bergeron and Strachan [2012] estimate that wintertime water vapor ( $H_2O_v$ ) emissions in Montreal exceed that of rural areas by over 50% due to combustion and sublimation/evaporation

of snow from roofs and roads, and Gorski et al. [2015] estimate that combustion  $\text{H}_2\text{O}_v$  can account for up to 13% of surface-level  $\text{H}_2\text{O}_v$  in Salt Lake City in winter.

In addition to instances of UME, annual maxima in greenhouse gas (GHG) mole fractions, such as for carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ), are observed in mid-latitude cities in winter when energy consumption is high, vertical mixing is poor, and boundary layer heights are low [Christen, 2014; Energy Information Administration (EIA), 2015; McKain et al., 2015; Moore and Jacobson, 2015]. Few studies have considered the impact of elevated mole fractions of  $\text{H}_2\text{O}_v$  and other GHGs on urban temperatures by absorption and re-emission of longwave radiation [Oke et al., 1991; Holmer and Eliasson, 1999; McCarthy et al., 2010]. UHI formation has been temporally linked with UME [Holmer and Eliasson, 1999; Deosthali, 2000; Kuttler et al., 2007]. Studies that have quantified the radiative impacts of GHGs on UHI intensity have considered the effect of increasing longwave radiation by  $40 \text{ Wm}^{-2}$  (informed by urban observations of the longwave contribution from GHGs) for idealized cities [Oke et al., 1991], as well as the impact of observed urban vapor pressure enhancements (3 hPa) on the Göteborg, Sweden UHI [Holmer and Eliasson, 1999], and the impact of increasing average global  $\text{CO}_2$  concentrations to 645 ppm on global megacity UHIs [McCarthy et al., 2010].

Understanding how urban emissions of  $\text{H}_2\text{O}_v$  and other GHGs influence the environment is important, as cities, despite covering only 3% of the Earth's land surface, are responsible for 70% of global  $\text{CO}_2$  emissions and house 54% of the world's population, with these numbers projected to grow in the coming decades [Center for International Earth Science Information Network, 2011; United Nations, 2011; World Health Organization, 2016]. A positive atmospheric  $\text{H}_2\text{O}_v$  feedback exists in response to increased  $\text{CO}_2$  concentrations, with models suggesting  $\text{H}_2\text{O}_v$  is responsible for a significant portion of warming via radiative effects [Rind et al., 1991; Willet et al., 2007]. Furthermore, it has been shown that atmospheric concentrations of  $\text{H}_2\text{O}_v$  are increasing and influence the rate of warming [Solomon et al., 2010; Chung et al., 2014]. However, questions still remain about local scale influences of  $\text{H}_2\text{O}_v$  emissions, and their magnitude.

Urban  $\text{H}_2\text{O}_v$  excess emissions could influence aerosol properties and the associated population of cloud condensation nuclei (CCN) which could also modify cloud cover and weather downwind of urban areas [Mölders and Olson, 2004; Kreidenweis et al., 2005; Bréon, 2006; Rosenfeld et al., 2008; Trusilova et al., 2008; Twohy et al., 2009; Kourtidis et al., 2015]. In

addition to regional effects on cloud cover and water cycling, enhanced  $\text{H}_2\text{O}_v$  mole fraction impacts the liquid water content of aerosols. As discussed in recent publications, aerosol liquid water content has a significant impact on the processing of pollutants that partition to the aerosol phase, or the evolution of secondary organic aerosol (SOA) and climate-relevant aerosol properties [Carlton and Turpin, 2013; Hodas *et al.*, 2014; Guo *et al.*, 2015; Nguyen *et al.*, 2015; Rindelaub *et al.*, 2015].

Here we discuss our airborne case studies of elevated  $\text{H}_2\text{O}_v$  mole fractions observed downwind of (1) the Washington, D.C.- Baltimore, MD, metropolitan area (D.C.-Balt), collected as part of the Wintertime Investigation of Emissions, Reactivity, and Transport (WINTER) and Fluxes of Atmospheric Greenhouse Gases in Maryland (FLAGG-MD) campaigns, and (2) Indianapolis, IN, as part of the ongoing Indianapolis Flux Experiment (INFLUX). Unlike past studies that have reported urban  $\text{H}_2\text{O}_v$  excess by comparing measurements from tower sites or surface-mobile traverses [Hage, 1975; Holmer and Eliasson, 1999; Deosthali, 2000; Richards, 2005; Kuttler *et al.*, 2007; Liu *et al.*, 2009; Hall *et al.*, 2016], this study represents the first reported observations and quantification of city-wide enhancements in  $\text{H}_2\text{O}_v$  mole fractions during daytime. Additionally, we report emission rates of urban-derived  $\text{H}_2\text{O}_v$  from our mass balance experiments conducted in the two cities, and discuss possible sources. We test the hypothesis that elevated  $\text{H}_2\text{O}_v$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  mole fractions within an urban center influence the UHI via direct radiative effects, and discuss potential impacts of urban  $\text{H}_2\text{O}_v$  emissions on areas within and downwind of cities.

## 2. Methods

### 2.1. Site Description

Airborne experiments were conducted above D.C.-Balt, the urban area centered around the cities of Washington, D.C. (38.905°N, 77.016°W) and Baltimore, MD (39.288°N, 76.617°W), on 13, 19, 20, 23, 25, 27 February and 9, 12 March, 2015 as part of the WINTER and FLAGG-MD campaigns. D.C.-Balt is a U.S. Census Bureau-defined Combined Statistical Area, and has a population of approximately 9.63 million [U.S. Census Bureau, 2016]. The population density across D.C.-Balt is spatially variable. The most densely populated areas, at 3806 persons km<sup>-2</sup> and 2174 persons km<sup>-2</sup>, are within the city boundaries of Washington, D.C. and Baltimore, MD, respectively, [US Census Bureau, 2010]. The urban study site is surrounded by rural land use to the north and south. The Appalachian Mountains lie to the west, and the Chesapeake Bay and Atlantic Ocean lie to the east of the urban area. Northwest winds were commonly observed during the D.C.-Balt flights, which is in line with long-term observations of wintertime winds in the area [Berg and Allwine, 2006]. The Washington National Airport reported average temperatures and winds speeds of -0.4°C and 4 m s<sup>-1</sup>, respectively, during the study period. Airborne observations of urban carbon monoxide, sulfur dioxide, nitrogen dioxide (NO<sub>2</sub>), ozone, and aerosol emissions from the D.C.-Balt area have been previously discussed [He et al., 2014; 2016; Brent et al., 2015].

Airborne experiments conducted by Purdue University in Indianapolis, IN (39.791°N, 86.148°W) have been ongoing since 2008 as part of the INFLUX campaign. Indianapolis and its surrounding urban/suburban sprawl have a population of approximately 1.99 million [US Census Bureau, 2016], and the population density is 914 persons km<sup>-2</sup> [US Census Bureau, 2010]. The Indianapolis flight experiments discussed herein were conducted in November of 2012 and 2014. The average monthly temperature in Indianapolis in November over these years was 4°C, and winds were from the southwest at 4 m s<sup>-1</sup> on average, as archived by the National Weather Service. Given its isolation from other urban areas, and its relatively simple meteorology and topography, Indianapolis is an ideal test bed for the development and evaluation of methods to quantify urban emissions from densely populated urban environments. Emissions of CO<sub>2</sub> and CH<sub>4</sub> from Indianapolis are discussed in Mays et al. [2009], Cambaliza et al. [2014, 2015], Lauvaux et al. [2016], and Heimbürger et al. [2017].

## 2.2. Aircraft Instrumentation

The two airborne platforms used to quantify GHG emissions from the urban areas were: Purdue University's Airborne Laboratory for Atmospheric Research (ALAR; <http://science.purdue.edu/shepson/research/bai/alar.html>) and the UMD's Cessna 402B research aircraft (<http://aosc.umd.edu/~flaggmd/>). Emission rates of urban H<sub>2</sub>O<sub>v</sub> excess for D.C.-Balt are estimated from data collected by both aircraft. Emission rates for Indianapolis are estimated from data collected by the ALAR. Table S1 is a flight log that details the date, city, aircraft, low and high temperature, and prior precipitation for all the flights discussed in this text. Purdue's ALAR and the UMD Cessna flew a coordinated flight (here on referred to as the inter-comparison flight) on 19 February 2015. The inter-comparison flight was designed for periods of the experiment to be flown in unison for measurement comparison. Figure S1 shows the ALAR and the UMD Cessna measurements of winds, temperature, pressure, and H<sub>2</sub>O<sub>v</sub> mole fraction (expressed as mmol mol<sup>-1</sup>) for a period of the inter-comparison flight in which the aircraft were flying parallel to one another, spaced ~1 km apart, and flying at the same altitude with their heading oriented perpendicular to the mean wind direction.

### 2.2.1. Purdue University's Airborne Laboratory for Atmospheric Research

Purdue's ALAR is a modified light twin-engine Beechcraft Duchess aircraft equipped with a Best Air Turbulence (BAT) probe for high frequency (50 Hz) three-dimensional wind measurements [Crawford and Dobosy, 1992; Garman *et al.*, 2006] installed at the nose of the aircraft. Temperature was measured using a Fast Ultra-Sensitive Temperature (FUST) probe installed on the underside of the BAT probe [Garman *et al.*, 2006]. Flight tracks were recorded using a global positioning system (GPS) and inertial navigation system (INS). During the course of the D.C.-Balt flights, the ALAR was equipped with several gas and aerosol analyzers including: (1) a Picarro G2301-m cavity ring-down spectrometer (CRDS) for 0.5 Hz CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O<sub>v</sub> measurements, (2) a Los Gatos Research (LGR) off-axis integrated cavity output spectrometer (OA-ICOS) for 1 Hz NO<sub>2</sub> measurements, and (3) an aerosol spectrometer (model 1.109, GRIMM Technologies, Inc., Douglasville, GA) for measurements (6 second intervals) of

particle concentration of diameters from 0.25 to 32  $\mu\text{m}$ . The  $\text{NO}_2$  and aerosol analyzers were not installed in ALAR at the time of the Indianapolis flight experiments reported here. Instrumentation was housed in a  $\sim 1 \text{ m}^3$  volume in the back of the aircraft. A blower installed at the rear of the aircraft pulled ambient air from the inlet at the nose of the aircraft through 5 cm Teflon tubing at a flow rate of  $1840 \text{ L min}^{-1}$ .

For Indianapolis flights, the ALAR Picarro CRDS was calibrated with an in-flight calibration system using National Oceanographic and Atmospheric Association (NOAA) Earth System Research Laboratory analytical standards. For D.C.-Balt flights, the ALAR Picarro CRDS was calibrated according to a Purdue-UMD cross-calibration with analytical  $\text{CO}_2$  and  $\text{CH}_4$  standards from the National Institute of Standards and Technology (NIST). For continuity, Purdue and UMD Picarro CRDS data collected during D.C.-Balt flights were calibrated using NIST standards. After the WINTER campaign, a dew point generator (model LI-610, LiCor Inc., Lincoln, NE) was used to compare saturation mole fractions to the CRDS  $\text{H}_2\text{O}_v$  measurements. The dew point generator has a reported precision of  $\pm 0.01^\circ\text{C}$  for dew point temperature set point. This equates to a maximum variability of  $\pm 8 \times 10^{-3} \text{ mmol mol}^{-1}$  in saturation mole fractions for the dew point temperatures measured. The CRDS-reported  $\text{H}_2\text{O}_v$  mole fractions were  $\sim 8\%$  lower than the saturation mole fractions for the set dew point temperatures. Purdue  $\text{H}_2\text{O}_v$  measurements were not calibrated for continuity with the UMD  $\text{H}_2\text{O}_v$  measurements (Figure S1). The Picarro G2301-m instrument has a measured precision of 0.03 ppm and 0.5 ppb for  $\text{CO}_2$  and  $\text{CH}_4$ , respectively (standard deviations ( $1\sigma$ ) of 0.5 Hz data over five minutes), for atmospherically relevant trace species mole fractions from dry analytical standards. The measured precision for  $\text{H}_2\text{O}_v$  when sampling humid air from the dew point generator is  $3 \times 10^{-2} \text{ mmol mol}^{-1}$  for relevant ambient  $\text{H}_2\text{O}_v$  mole fractions. This value is a combination of the precision of the dew point generator output (maximum variability of  $\pm 8 \times 10^{-3} \text{ mmol mol}^{-1}$ ) and the CRDS instrument precision.

#### 2.2.2. University of Maryland's Cessna 402B Research Aircraft

The UMD operated a Cessna 402B research aircraft equipped with an instrument package to measure gaseous and particle pollutants [He *et al.*, 2014, 2016]. Separate inlets for gases and



particles, as well as temperature and humidity sensors were installed at the nose of the aircraft. Temperature, humidity, and pressure were measured using a Vaisala probe (Model PTU300, Vaisala Inc., Woburn, MA). Flight tracks were recorded using a handheld GPS and an aircraft INS. Horizontal two-dimensional wind speed was calculated by a Garmin G600 system using information from an INS, GPS, and an air data computer (Model GTN650, Garmin, Chicago, IL). The UMD Cessna research aircraft was equipped with a suite of trace gas and aerosol analyzers. Those relevant to this study include a Picarro G2401-m CRDS for 0.5 Hz CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>O<sub>v</sub> measurements, and an LGR OA-ICOS for 1 Hz NO<sub>2</sub> measurements [Brent *et al.*, 2015].

For the flights in D.C.-Balt, the UMD Picarro CRDS was calibrated both on the ground and in the air with analytical standards from NIST. The Picarro G2401-m instrument has measured precisions of 0.02 ppm for CO<sub>2</sub>, 0.2 ppb for CH<sub>4</sub>, and 4 ppb for CO (standard deviations (1 $\sigma$ ) of 0.5 Hz data over five minutes) for atmospherically relevant trace species mole fractions measured from dry analytical standards. The manufacturer-reported H<sub>2</sub>O<sub>v</sub> precision is 1  $\times 10^{-2}$  mmol mol<sup>-1</sup> for humid air samples.

### 2.3. Mass Balance Flight Design

Airborne mass balance experiments were performed with the Purdue and the UMD aircraft to quantify citywide GHG emissions from Indianapolis and D.C.-Balt [Trainer *et al.*, 1995; Kalthoff *et al.*, 2002; Mays *et al.*, 2009; Karion *et al.*, 2013, 2015; Gioli *et al.*, 2014; O'Shea *et al.*, 2014; Petron, *et al.*, 2014; Cambaliza *et al.*, 2014, 2015; Lavoie, *et al.*, 2015; Heimbürger *et al.*, 2017]. Alternative airborne methods for estimating urban fluxes of energy, greenhouse gases, and other anthropogenic pollutants have been reported [Font *et al.*, 2015; Karl *et al.*, 2009; Trousdel *et al.*, 2016; Vaughan *et al.*, 2016]. In an airborne mass balance experiment, transects are flown upwind and downwind of an emission source, D.C.-Balt or Indianapolis, and the emission rate of the species of interest, H<sub>2</sub>O<sub>v</sub>, is calculated from the urban enhancement in mole fraction relative to background and the perpendicular component of the wind speed relative to the flight track. Figure 1a-b shows the ALAR's flight path and altitude, respectively, during the 27 February 2015 D.C.-Balt mass balance flight. The 27 February 2015

flight is used throughout the paper as a representative example of an urban mass balance flight for which an urban  $\text{H}_2\text{O}_v$  excess signal is observed. Flight paths from the remaining mass balance flights are provided in Figure S2. All flights commenced at approximately noon to minimize atmospheric boundary layer growth throughout the duration of the flight [Stull, 1988], consistent with our observations. Typically, a vertical profile was flown on the upwind side of the city to characterize the atmospheric boundary layer, followed by an upwind transect to measure the  $\text{H}_2\text{O}_v$  mole fraction entering the study area. Next, downwind transects were flown at different altitudes approximately equally spaced throughout the boundary layer, (Figure 1b). Downwind transects were conducted approximately 30 km and 70 km from the center of Indianapolis and D.C.-Balt, respectively. Downwind transect locations are chosen so that emissions have time to mix through the boundary layer. While this results in a lower uncertainty in the calculated results, our analysis makes no assumptions about a well-mixed boundary layer. The locations of D.C.-Balt downwind transects were also in part dictated by flight restrictions. The number of downwind transects completed in each flight was dependent on city size and the time available before the atmospheric boundary layer became stable. The downwind transects were designed to extend several tens of kilometers beyond the horizontal bounds of the urban area to ensure complete sampling of the urban plume, and appropriate sampling of background  $\text{H}_2\text{O}_v$  mole fractions at the lateral edges of the downwind transects. For most flights, a second vertical profile was flown downwind of the city to determine boundary layer depth evolution, as well as characterize vertical mixing downwind of the metropolitan area.

## 2.4. Background Determination

One of the objectives of this study is to determine urban emission rates of  $\text{H}_2\text{O}_v$  *in excess* of the surrounding rural area. A background concentration serves as a reference for determining the incremental urban enhancement in  $\text{H}_2\text{O}_v$  mole fraction, and is ideally representative of air not influenced by the urban area, but of the same air mass as the air sampled downwind of the urban center. To determine the incremental urban enhancement in  $\text{H}_2\text{O}_v$  relative to the surrounding rural areas, background  $\text{H}_2\text{O}_v$  mole fractions were defined from air sampled along the lateral edges of the downwind transects where mole fractions are relatively constant, and are likely a

result of rural influence only. This approach has been used in aircraft mass balance experiments to quantify CH<sub>4</sub> and CO<sub>2</sub> emissions from cities and natural gas fields [Cambaliza *et al.*, 2014, 2015; Karion *et al.*, 2015; Heimbürger *et al.*, 2017]. Measurements of H<sub>2</sub>O<sub>v</sub> mole fraction made along upwind transects were used to identify spatial variability in H<sub>2</sub>O<sub>v</sub> mole fraction entering the study areas.

Figure 2 shows the urban H<sub>2</sub>O<sub>v</sub> plume intercepted downwind of D.C.-Balt on 27 February 2015 (plume profiles from the remaining flight days are shown in Figure S2). A line (cyan in Figure 2) connecting the baseline H<sub>2</sub>O<sub>v</sub> mole fractions at either ends of the transects defines the background mole fraction at each data point sampled along the urban plume. Downwind transects were flown well past the boundaries of the urban area, so that air sampled near transect ends did not pass over urbanized areas, and were thus representative of background (rural) mole fractions at the time and location the downwind transect was flown. We define the transition from rural-influenced air to urban-influenced air as the location that the downwind H<sub>2</sub>O<sub>v</sub> mole fractions are greater than the background mole fraction plus three times the standard deviation of the background. The standard deviation in H<sub>2</sub>O<sub>v</sub> mole fraction along the upwind transect is used as a proxy for defining the standard deviation of the background, assuming that variability in H<sub>2</sub>O<sub>v</sub> mole fraction along the upwind transect would be similar to the variability in downwind H<sub>2</sub>O<sub>v</sub> mole fraction not influenced by the urban area. This criterion (background plus three standard deviations of the background) is also used for determining if an urban H<sub>2</sub>O<sub>v</sub> excess signal exists (as indicated in Table S1).

H<sub>2</sub>O<sub>v</sub> mole fractions observed upwind of the urban areas (red trace in Figure 2) were often similar in magnitude to the linear, transect-edge-defined background (cyan trace in Figure 2). Instances when transect-edge-defined background H<sub>2</sub>O<sub>v</sub> mole fractions were higher or lower relative to upwind mole fractions could indicate that the surrounding rural area acted as a source of moisture or there was entrainment of drier free tropospheric air, respectively. We have previously determined that upwind transects do not provide a reliable background measurement for mass balance experiments, but rather, that the rural edges of the downwind transects provide a more reliable background, in part because the measurements on the transect edges are conducted closer in time to urban plume sampling [Cambaliza *et al.*, 2014, Karion *et al.*, 2015, Heimbürger *et al.*, 2017]. Measurements of background mole fraction for all flights when an

urban H<sub>2</sub>O<sub>v</sub> excess signal was observed are explained in detail in the captions of Figure S2.1-7 in the Supporting Information (SI).

## 2.5. Emission Rate Calculation

To quantify the emission rate of urban H<sub>2</sub>O<sub>v</sub> excess from D.C.-Balt and Indianapolis, the flux,  $F_{Urban,ij}$ , of urban H<sub>2</sub>O<sub>v</sub> excess is calculated at each downwind data point (unique distance along the downwind track ( $i$ ) and altitude ( $j$ )), according to Equation 1.

$$F_{Urban,ij} = U_{\perp,ij} \cdot (H_2O_{v,dw,ij} - H_2O_{v,bg,ij}) \quad (1)$$

For Equation 1, reported H<sub>2</sub>O<sub>v</sub> mole fractions have been converted to molar density (mol m<sup>-3</sup>) using the ideal gas law, and simultaneous pressure and temperature measurements (an expanded form of Equation 1 is in the SI). The background mole fraction (Section 2.4),  $H_2O_{v,bg,ij}$ , is subtracted from the corresponding downwind H<sub>2</sub>O<sub>v</sub> mole fraction,  $H_2O_{v,dw,ij}$ , giving an urban enhancement in H<sub>2</sub>O<sub>v</sub>. The H<sub>2</sub>O<sub>v</sub> enhancement is multiplied by the perpendicular component of the wind speed (50 Hz winds averaged over 10 seconds),  $U_{\perp,ij}$  (m s<sup>-1</sup>). The result is an urban H<sub>2</sub>O<sub>v</sub> excess flux (mol m<sup>-2</sup> s<sup>-1</sup>),  $F_{Urban,ij}$ , calculated at each data point sampled downwind of the urban center as shown in Figure 3.

To determine the percent contribution of urban-derived H<sub>2</sub>O<sub>v</sub> to the total transport (background + urban excess) of atmospheric boundary layer H<sub>2</sub>O<sub>v</sub> exiting the urban area, the total H<sub>2</sub>O<sub>v</sub> flux,  $F_{Total,ij}$ , at any point is calculated according to Equation 2. Equation 2 is identical to Equation 1, except that a background mole fraction,  $H_2O_{v,bg,ij}$ , is not subtracted from the downwind H<sub>2</sub>O<sub>v</sub> mole fractions,  $H_2O_{v,dw,ij}$ .

$$F_{Total,ij} = U_{\perp,ij} \cdot H_2O_{v,dw,ij} \quad (2)$$

The flux values defined at each downwind point,  $F_{Urban,ij}$  and  $F_{Total,ij}$ , are used as inputs to a kriging program (MATLAB EasyKrig3.0) to interpolate/extrapolate a two-dimensional x-z plane, or matrix, of downwind H<sub>2</sub>O<sub>v</sub> fluxes,  $M_{Urban}$  or  $M_{Total}$  [Mays *et al.*, 2009; Cambaliza *et al.*, 2014, 2015]. The flux matrices are gridded at a resolution of 100 m (x

dimension) x 10 m (z dimension), from the surface to the top of the boundary layer. We define boundary layer depth ( $z_i$ ) as the altitude along the vertical profile associated with the greatest change in potential temperature (maximum  $d\theta/dz$ , where  $\theta$  is potential temperature) [Cambaliza *et al.*, 2014]. Vertical profiles with indicated boundary layer height for each day are provided in the SI. The citywide  $H_2O_v$  emission rate,  $ER_{Urban}$  ( $\text{mol s}^{-1}$ ; reported in units of  $\text{kg s}^{-1}$ ), is calculated by integrating the urban  $H_2O_v$  excess flux matrix,  $M_{Urban}$ , across the horizontal bounds of the city, and vertically from the surface to the top of the boundary layer ( $z_i$ ) according to Equation 3:

$$ER_{Urban \text{ or } Total} = \int_0^{z_i} \int_{-x}^{+x} M_{Urban \text{ or } Total} dx dz \quad (3)$$

Similarly, the total  $H_2O_v$  transport emission rate ( $ER_{Total}$ ) is calculated according to Equation 3 by integrating over the total  $H_2O_v$  flux matrix,  $M_{Total}$ . In principle, the uncertainty in the ratio of urban  $H_2O_v$  excess to the total  $H_2O_v$  transport through the study area ( $ER_{Urban}:ER_{Total}$ ) would be smaller than the uncertainty of the individual emission rates because the wind speed and kriging uncertainties would be effectively canceled. An uncertainty analysis of the mass balance emission rate calculation is provided in the SI.

### 3. Results and Discussion

#### 3.1. Urban H<sub>2</sub>O<sub>v</sub> Enhancements and Emission Rates

An elevated urban H<sub>2</sub>O<sub>v</sub> signal was observed on five (13 February, 20 February, 27 February, 9 March, and 12 March 2015) of the eight flights conducted around D.C.-Balt. An urban H<sub>2</sub>O<sub>v</sub> excess signal was not observed on 19 February, 23 February, or 25 February 2015 in D.C.-Balt. Figure S4 shows flight paths and observations of upwind and downwind H<sub>2</sub>O<sub>v</sub> mole fractions for these days. Between March 2011 to December 2014, an urban H<sub>2</sub>O<sub>v</sub> excess signal was observed on two of 16 mass balance flights conducted in Indianapolis during non-growing season months (November through March).

The magnitude of the urban H<sub>2</sub>O<sub>v</sub> signal varied by day and, for some flights, by altitude depending on the extent of vertical mixing within the boundary layer. The boundary layer downwind of D.C.-Balt was poorly mixed on 27 February 2015 as the magnitude of the H<sub>2</sub>O<sub>v</sub>, CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>2</sub>, and aerosol plumes are altitude dependent (Figure 2; Figure 4a-e). The highest downwind transect conducted on 27 February 2015 is shorter than the lower two downwind transects (Figure 2-4) because the aircraft had to stop to refuel. Data collected after refueling (Figure 1b) on 27 February 2015 is not used in our analysis because large variability in H<sub>2</sub>O<sub>v</sub> and other GHG mole fractions was observed along the remainder of the final downwind transect. This variability is characteristic of mixed layer decay observed in late afternoon or early evening [Acevedo and Fitzjarrald, 2001; Lothon et al., 2014]. The maximum urban enhancement in H<sub>2</sub>O<sub>v</sub> mole fraction, 1.5 mmol mol<sup>-1</sup>, was observed on the lowest downwind transect (390 m above sea level (msl)) of the 27 February 2015 flight. The maximum enhancement in H<sub>2</sub>O<sub>v</sub> mole fraction ranged between 0.24 mmol mol<sup>-1</sup> – 1.5 mmol mol<sup>-1</sup> for the five D.C.-Balt flights. An urban H<sub>2</sub>O<sub>v</sub> excess signal of 0.72 mmol mol<sup>-1</sup> and 0.65 mmol mol<sup>-1</sup> was observed on two mass balance flights conducted in Indianapolis on 8 November 2012 and 25 November 2014, respectively. Both the presence and magnitude of the urban H<sub>2</sub>O<sub>v</sub> excess signals in D.C.-Balt and Indianapolis exhibited inter-day variability, and were not necessarily proportional to city size (e.g. the observed Indianapolis H<sub>2</sub>O<sub>v</sub> excess signals were sometimes greater than the D.C.-Balt signals). Maximum urban H<sub>2</sub>O<sub>v</sub> enhancements for the D.C.-Balt and Indianapolis flights can be found in Table 1.

Urban emission rates, calculated according to Equations 1 and 3, ranged from 1.6 (±0.66) × 10<sup>4</sup> – 1.7 (±0.81) × 10<sup>5</sup> kg H<sub>2</sub>O<sub>v</sub> s<sup>-1</sup> for D.C.-Balt and 2.1 (±1.2) × 10<sup>4</sup> – 3.5 (±1.4) × 10<sup>4</sup> kg

$\text{H}_2\text{O}_v \text{ s}^{-1}$  for Indianapolis. Urban  $\text{H}_2\text{O}_v$  excess emission rates are reported in Table 1. Uncertainties associated with the calculation of citywide emission rates were estimated on average to be 46% ( $1\sigma$ ; range: 39% - 59%), and are discussed in the SI. The percent contribution of urban  $\text{H}_2\text{O}_v$  excess to the total flow (background + urban excess; discussed in Methods Section 2.5) of atmospheric boundary layer  $\text{H}_2\text{O}_v$  out of the study areas range from 1.5 – 8.4% (average: 4.1%) for the D.C.-Balt flights, and average 2.8% for the Indianapolis flights (Table 1).

It is important to note that this range of emission rates is not representative of every mass balance flight flown around the D.C.-Balt and Indianapolis areas, rather the range corresponds only to days when an urban  $\text{H}_2\text{O}_v$  excess was observed. Our observations of urban  $\text{H}_2\text{O}_v$  excess occurred during winter, when transpiration rates and saturation vapor pressure are lower than in summer months. During this time period, urban  $\text{H}_2\text{O}_v$  excess signals may be easier to observe relative to the noise, or natural variability in  $\text{H}_2\text{O}_v$  mole fractions. There were three of eight D.C.-Balt flight days and 14 of 16 Indianapolis mass balance flights on which the downwind  $\text{H}_2\text{O}_v$  mole fractions were approximately equal to, or less than, the observed upwind  $\text{H}_2\text{O}_v$  mole fractions. Sisterson and Dirks [1978] measured lower specific humidity values along airborne transects downwind of St. Louis, Missouri in summertime, relative to upwind transects. Sisterson and Dirks [1978] hypothesize decreased rates of evapotranspiration within the city and UHI-induced entrainment contributed to lower downwind specific humidity.

### 3.2. Spatial Correlation with Anthropogenic Pollutants

Figure 4a-e shows that the plume shapes and widths of the other anthropogenic species,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}_2$ , and aerosol number concentration, respectively, track the urban  $\text{H}_2\text{O}_v$  plume. Periods without  $\text{NO}_2$  data in Figure 4d correspond to times the analyzer was performing five-minute-long internal zeroes (every 30 minutes of sampling). Similar urban plume shapes of  $\text{H}_2\text{O}_v$  and other anthropogenic species were observed during the other D.C.-Balt flights (Figure S2.3-7). Additionally, the most intense  $\text{H}_2\text{O}_v$  peak observed downwind of the D.C.-Balt area on 27 February 2015 is co-located with the urban aerosol plume and the greatest aerosol concentrations as shown in Figure 4f-g. Aerosol number concentration increased three to fourfold after passing over D.C.-Balt, with little growth observed in aerosol diameter (Figure 4f-g). Hygroscopic aerosol with diameters greater than  $\sim 0.1 \mu\text{m}$  can act as CCN, and elevated aerosol concentrations can produce smaller and more numerous droplets that take longer to grow to precipitation size

droplets under constant moisture conditions, impacting cloud optical properties and precipitation yield and frequency [Kreidenweis *et al.*, 2005; Bréon, 2006]. However, if aerosol emissions are collocated with H<sub>2</sub>O<sub>v</sub> emissions, as indicated by the present observations (Figure 4a, e-g), moisture conditions would not be constant, and may counteract aerosol-delayed precipitation [Rosenfeld *et al.*, 2008]. Indeed, it has also been shown that H<sub>2</sub>O<sub>v</sub> can have a stronger impact on cloud cover than aerosol optical depth [Kourtidis *et al.*, 2015].

The downwind enhancements of the combustion products CO<sub>2</sub>, H<sub>2</sub>O<sub>v</sub>, and NO<sub>2</sub> were atmospherically correlated (Pearson correlation coefficient of 0.83 for CO<sub>2</sub> and H<sub>2</sub>O<sub>v</sub>) during the 27 February 2015 flight (Figure 5). This correlation was also observed for three of the other D.C.-Balt flights, but to a lesser extent ( $r = 0.41 - 0.50$ ). There was one D.C.-Balt flight day, 9 March 2015, where no correlation ( $r = 0.1$ ) was observed. Figure S5 shows correlation plots of combustion product enhancements for the remaining D.C.-Balt flight days when an urban H<sub>2</sub>O<sub>v</sub> excess signal was observed. This implies that the urban H<sub>2</sub>O<sub>v</sub> excess is frequently associated spatially and temporally with anthropogenic activities within D.C.-Balt. While the observed urban plumes of H<sub>2</sub>O<sub>v</sub>, CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>2</sub>, and aerosol track a similar shape (Figure 4a-e) on 27 February 2015 in D.C.-Balt, and H<sub>2</sub>O<sub>v</sub>, CO<sub>2</sub>, and NO<sub>2</sub> enhancements show correlation of varying strengths (Figure 5, S5) data from the Indianapolis flights do not always suggest an equally strong spatial correlation between these species. Figure 6a-c shows urban plume profiles of H<sub>2</sub>O<sub>v</sub>, CO<sub>2</sub>, and CH<sub>4</sub>, respectively, from the 8 November 2012 flight in Indianapolis (flight path shown in Figure S2.1a). The urban H<sub>2</sub>O<sub>v</sub> plume was observed to be slightly broader, and did not exhibit the same double peak profile of the CO<sub>2</sub> and CH<sub>4</sub> plumes during the 8 November 2012 flight. Similarly, the H<sub>2</sub>O<sub>v</sub> plume observed on the 25 November 2014 flight is offset to the south of the CH<sub>4</sub> and CO<sub>2</sub> plumes (Figure 6d-f, respectively; flight path shown in Figure S2.2a). In the case of the observations from 25 November 2014, it appears that the urban H<sub>2</sub>O<sub>v</sub> plume is originating from the southern outskirts of Indianapolis, which is primarily suburban. The largest CO<sub>2</sub> and CH<sub>4</sub> plumes appear to originate slightly south of central Indianapolis, likely as a result of emissions from the city's power plant and landfill, which are located in the southwest part of the city. Potential reasons for differences in observed spatial relationships between these atmospheric species of urban origin are discussed in Section 3.3.3.



### 3.3. Sources and Impacts of Urban H<sub>2</sub>O<sub>v</sub> Excess

Below we discuss sources and conditions likely contributing to the enhancement in H<sub>2</sub>O<sub>v</sub> mole fractions observed downwind of the D.C.-Balt and Indianapolis areas, including direct anthropogenic moisture sources such as combustion and evaporative cooling, moisture contributions from local bodies of water, which we believe to be negligible, and finally, differences in urban and rural evaporation rates. Lastly, we consider the radiative impact of elevated H<sub>2</sub>O<sub>v</sub> and GHG mole fractions on the urban boundary layer, more specifically UHI intensity.

#### 3.3.1. Direct Anthropogenic Sources

Combustion sources have been identified as a major wintertime contributor to urban moisture in mid-latitude cities, contributing up to 13% of surface-level moisture during inversion periods in Salt Lake City, UT, and causing urban low-temperature fog in Edmonton, Alberta, Canada [Hage, 1972, 1975; Ackerman, 1987; Gorski *et al.*, 2015]. To estimate the contribution of H<sub>2</sub>O<sub>v</sub> from combustion sources, CO<sub>2</sub> emission rates calculated according to the procedure described in the Methods Sections 2.4-5, were multiplied by a H<sub>2</sub>O<sub>v</sub>:CO<sub>2</sub> combustion ratio weighted for the fossil fuel use distribution in the D.C.-Balt area [EPA, 2015; EIA, 2015]. The calculation of the consumption-weighted H<sub>2</sub>O<sub>v</sub>:CO<sub>2</sub> combustion ratio, estimated to be approximately 1.2 H<sub>2</sub>O:1 CO<sub>2</sub>, is discussed in the SI. Heating and electricity generation via fossil fuel combustion (electricity generation from nuclear power is also significant in the area) in the D.C.-Balt study area is mainly achieved through the burning of coal and natural gas. Petroleum is rarely used for heating or electricity generation in the area, and is mainly consumed by the transportation sector after it has been processed into gasoline [EIA, 2016a]. The magnitude of the combustion-derived H<sub>2</sub>O<sub>v</sub> emission rates, presented as ER<sub>Combustion</sub> in Table 2, appear to be inversely proportional to temperature, as we expect in the winter due to increased fossil fuel consumption for space-heating. Also presented in Table 2 is the contribution of combustion-derived H<sub>2</sub>O<sub>v</sub> to the urban H<sub>2</sub>O<sub>v</sub> excess signal, which was estimated to range from 1.0-9.6%. However, the maximum contribution of combustion-derived H<sub>2</sub>O<sub>v</sub> to the total flow of H<sub>2</sub>O<sub>v</sub>

exiting the study area is negligible, with a maximum contribution of ~0.32%. Similar to our analysis, Kalanda et al. [1980] report high urban latent heat fluxes, but estimate the maximum combustion-derived  $\text{H}_2\text{O}_v$  contribution to be at least an order of magnitude lower than the observed latent heat fluxes. Given our combustion-derived  $\text{H}_2\text{O}_v$  estimates, it is likely that the observed correlation between combustion products  $\text{CO}_2$ ,  $\text{H}_2\text{O}_v$ , and  $\text{NO}_2$  shown in Figure 5 (and Figure S5a,b,d) represents spatial coherence between combustion sources and the sources of urban-derived  $\text{H}_2\text{O}_v$  in D.C.-Balt on some days. The observed combustion product correlation on 9 March 2015 (Figure S5c) does not show as strong a relationship as the other D.C.-Balt days. Additionally, the plume shapes of  $\text{H}_2\text{O}_v$  and  $\text{CO}_2$  from Indianapolis in Figure 6 do not track one another, indicating that combustion sources are not the dominant source of urban  $\text{H}_2\text{O}_v$  excess for these days.

In addition to the  $\text{H}_2\text{O}_v$  produced from combustion reactions, the other main form of direct anthropogenic moisture is from the phase change associated with evaporative cooling equipment [Sailor, 2011]. Evaporative cooling from air conditioning systems was implicated as the major contributor to large summertime latent heat fluxes in Tokyo, Japan by Moriwaki et al. [2008]. However, the authors report winter urban latent heat fluxes to be nearly two orders of magnitude lower than their summer estimates. Evaporative cooling towers from energy generating stations are sources of direct anthropogenic moisture throughout the year. Latent heat flux contributions from cooling towers are often not included in urban energy balance modeling because there are few quantitative reports on their contribution, and these estimates tend to be small [Grimmond et al., 2010]. Cooling tower plume dispersion models have been evaluated with empirical data collected by the EPA and United States national labs during the 1970s [Meroney, 2006; Ruiz et al., 2013]. Stockham [1971] reports periodic  $\text{H}_2\text{O}_v$  emissions over a four-month period from the cooling towers of a coal-fired 1,800 MW electricity generation facility. From the data reported by Stockham [1971], the linear relationship ( $R^2 = 0.983$ ,  $N=11$ ) between the cooling tower  $\text{H}_2\text{O}_v$  emission rate and the capacity at which the facility was operating was determined to be  $4.1 \text{ g H}_2\text{O}_v \text{ s}^{-1} \text{ MW}^{-1}$  for every percent of operating capacity. Orville et al. [1981] simulated emissions to be  $2.5 \times 10^4 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$  from a 48,000 MW power park using an unspecified fuel source. Hane [1978] simulated slightly higher emissions,  $3 \times 10^4 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$ , from a nuclear plant, but did not specify the plant's power output. The power plants within the D.C.-Balt study area were capable of collectively generating ~15,700 MW of power

during Winter 2015, and the primary fuel source was coal for most of the facilities [EIA, 2016b]. By applying the operating capacity-emission rate relationship observed by Stockham [1971] to the D.C.-Balt electricity generating facilities, we estimate the cooling towers within the study area would emit  $\sim 6.5 \times 10^3 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$  if operating at full capacity. Similarly, scaling Orville et al. [1981]'s emissions by power output for the D.C.-Balt facilities results in a maximum emission rate of  $8.2 \times 10^3 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$ . Averaging the cooling tower emission estimates based on Stockham [1971] and Orville et al. [1981] gives a maximum collective cooling tower emission rate of  $7.4 \times 10^3 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$  for D.C.-Balt. Repeating this calculation for the energy generating facilities' cumulative power output of 1,400 MW in Indianapolis, gives a maximum cooling tower emission rate of  $6.7 \times 10^2 \text{ kg H}_2\text{O}_v \text{ s}^{-1}$ . Given these operating conditions, cooling tower  $\text{H}_2\text{O}_v$  emissions could contribute up to  $\sim 43\%$  of the urban excess  $\text{H}_2\text{O}_v$  signal for the D.C.-Balt flight day with the smallest observed emission rate,  $1.60 \times 10^4 \text{ kg s}^{-1}$  on 13 February 2015. However, assuming the same operating conditions, cooling tower  $\text{H}_2\text{O}_v$  emissions would only contribute  $\sim 4\%$  to the maximum observed urban excess  $\text{H}_2\text{O}_v$  emission rate of  $1.68 \times 10^5 \text{ kg s}^{-1}$  on 27 February 2015 in D.C.-Balt. Similarly, cooling tower emissions from energy generating facilities operating at full capacity in Indianapolis would only contribute approximately 3% and 2% to the urban  $\text{H}_2\text{O}_v$  excess signal observed on 8 November 2012 and 25 November 2014, respectively. Maximum cooling tower emission rate estimates and their contribution to the observed urban  $\text{H}_2\text{O}_v$  excess signals are provided in Table 2.

### 3.3.2. Contribution from Local Bodies of Water

Due to the proximity of the D.C.-Balt area to the Atlantic Ocean, it is possible that moist air parcels originating from the sea-breeze were sampled aloft on their return circulation toward the ocean [Stull, 1988]. However, moist sea-breeze air would likely contribute to humidity levels equally along the coast, and not contribute preferentially to urban air than rural air. A sea-breeze circulation was not observed on 27 February 2015, as the wind direction measured along the lowest (390 msl) downwind transect originated from the northwest (Figure S6), nor was it observed during the other D.C.-Balt flight days.

The Chesapeake Bay, across which downwind transects were sometimes flown, was frozen for the majority of the WINTER field campaign (Figure S7). We note that the vapor pressure of ice is only slightly lower than that of liquid water at the same temperature. We believe it is unlikely that there was a significant contribution of moisture from the Chesapeake Bay considering the well-defined  $\text{H}_2\text{O}_v$  plumes intercepted directly downwind of the D.C.-Balt area (Figure 1a; Figure S2.3-7), rather than broad plumes spanning the length of the Chesapeake Bay as would be expected if the Chesapeake was the excess  $\text{H}_2\text{O}_v$  source. The most intense plume of excess  $\text{H}_2\text{O}_v$  observed on 27 February 2015 was in fact upwind of the Chesapeake Bay (Figure 1a). We note again that the urban  $\text{H}_2\text{O}_v$  excess signal is often correlated temporally and spatially with anthropogenic activities, as demonstrated by the combustion product correlation plots for most of the flights in D.C.-Balt (Figure 5; Figure S5). Additionally, an urban  $\text{H}_2\text{O}_v$  excess signal has been observed downwind of Indianapolis (Figure 6; Figures S2.1-2), in the absence of significant bodies of water. Relative to D.C.-Balt, Indianapolis is a meteorologically simple environment, and the nearest body of water, Lake Michigan, is over 200 km north of the city.

### 3.3.3. Urban-Rural Energy Balance Differences

Our estimates indicate that the combined emissions from combustion sources and cooling towers at most account for approximately half of the observed enhancement in  $\text{H}_2\text{O}_v$  mole fractions in the outflow from D.C.-Balt and Indianapolis. Additionally, we infer from our observations that nearby bodies of water did not contribute to the observed  $\text{H}_2\text{O}_v$  enhancement in

the D.C.-Balt or Indianapolis outflows. Additional sources of urban-derived  $\text{H}_2\text{O}_v$  must have contributed to the enhancement in urban  $\text{H}_2\text{O}_v$  outflow on the days when an elevated urban  $\text{H}_2\text{O}_v$  signal was observed. High latent heat fluxes have been reported within urban areas, particularly following precipitation events, by several urban energy balance studies [Oke, 1979; Kalanda *et al.*, 1980; Oke and McCaughey, 1983; Grimmond, 1992; Oke *et al.*, 1992; Offerle *et al.*, 2006; Ward *et al.*, 2013; Ramamurthy *et al.*, 2014; Ao *et al.*, 2016]. Rapid urban evaporation, providing there is available moisture, can result from the oasis effect, a local or microscale advection process that occurs when warmer or drier air is advected from above an impervious surface to a moist and/or porous surface creating a large moisture gradient, initiating faster rates of evaporation and snowmelt [Oke, 1979; Bengtsson and Westerström, 1992; Neumann and Marsh, 1998; Moriwaki and Kanda, 2004]. The northeastern United States received significant amounts of snow and rain throughout the WINTER campaign. Over the one month of Purdue and UMD mass balance flights (13 February to 12 March 2015), the D.C.-Balt area received approximately 101 mm of precipitation (reported by Washington National and Baltimore-Washington International Airports). From 1 January to 12 March 2015 (date of last D.C.-Balt mass balance flight), the D.C.-Balt area received approximately 29 mm more precipitation than average (snow accumulation is converted to snow water equivalent). The oasis effect could be a contributor to the observed urban  $\text{H}_2\text{O}_v$  excess signals. We note that our observations indicate that prior precipitation does not necessarily lead to an observable urban  $\text{H}_2\text{O}_v$  excess signal. Similar amounts of snow fell in D.C.-Balt prior to all flight days, including days when an urban  $\text{H}_2\text{O}_v$  excess signal was not observed (Table S1). While our measurements do not allow us to comment on the conditions impacting urban evaporation rates, other studies have shown that wintertime urban latent heat fluxes are sensitive to the physical state and availability of water on and within impervious and natural land cover [Offerle *et al.*, 2006; Lemonsu *et al.*, 2008; Leroyer *et al.*, 2010; Bergeron and Strachan, 2012].

In addition to being influenced by micro- and local scale advection processes, rates of evaporation and urban snowmelt can be influenced by large anthropogenic sensible heat fluxes in areas where space-heating occurs [Bengtsson and Westerström, 1992; Grimmond, 1992; Sailor, 2011; Bergeron and Strachan, 2012]. It is possible that anthropogenic heat fluxes during the D.C.-Balt flights were significant considering the sub-zero temperatures (Table 2) and space heating that would be required. Urban snowmelt has also been shown to be influenced by

longwave radiation emitted from buildings with high emissivity values, and the relatively lower albedo of the surrounding urban surfaces [Lemonsu *et al.*, 2008; Leroyer *et al.*, 2010; Bergeron and Strachan, 2012]. Urban snow typically is cleared from parking lots, roads, and sidewalks and gathered in large piles [Järvi *et al.*, 2014], where it can become packed and mixed with gravel and dirt, significantly lowering its albedo [Bengtsson and Westerström, 1992; Ho and Valeo, 2005]. The effect of road salt on evaporation within cities is complex. Road salt helps to melt ice and snow on roadways by decreasing the freezing point of water, but the resulting salt-meltwater solution has a vapor pressure lower than that of pure water.

At present, our measurements cannot explain why the urban  $\text{H}_2\text{O}_v$  excess signal is observed on some days, but not others. Our estimates indicate that combustion and cooling tower emissions cannot entirely account for the magnitude of the observed urban  $\text{H}_2\text{O}_v$  signals. Indeed, if combustion and cooling tower emissions were dominant sources, we would expect elevated urban  $\text{H}_2\text{O}_v$  mole fractions to be observed on every flight. But this is not the case for the D.C.-Balt flight days on 19, 23, and 25 February 2015 when an elevated urban  $\text{H}_2\text{O}_v$  signal was not observed (Figure S4). If enhanced urban snowmelt and evaporation is widespread, i.e. on the city-scale, it could be a dominant urban  $\text{H}_2\text{O}_v$  excess source. It is likely that some combination of abundant moisture, anthropogenic heat flux, radiative properties of urban surfaces, and local-scale advection processes resulted in the urban areas acting as sources of indirect anthropogenic  $\text{H}_2\text{O}_v$ . Enhanced rates of urban evaporation and snowmelt could be responsible for the sometimes spatially offset urban  $\text{H}_2\text{O}_v$  plume relative to the plumes of other GHGs (Figure 6 and Figure S5c). For example, emissions of  $\text{CO}_2$  and  $\text{CH}_4$  from power plants, transportation, natural gas distribution networks, and landfills are concentrated at the center of Indianapolis [Cambaliza *et al.*, 2014], but significant advection-assisted evaporation could occur along the highways and residential areas surrounding the urban center. Bergeron and Strachan [2012] report different wintertime  $\text{H}_2\text{O}_v$  emission responses from urban and suburban tower sites within 18 km of one another in Montreal. Our measurements allow for city-wide estimates of urban  $\text{H}_2\text{O}_v$  excess emissions relative to rural areas. To determine if rapid evaporation and snowmelt is a dominant contributor to the urban  $\text{H}_2\text{O}_v$  excess signal on the city-scale, future studies should conduct mobile measurements of urban-rural humidity differences [Chandler, 1967; Kopec, 1973; Bornstein and Tam, 1977; Sisterson and Dirks, 1978; Richards, 2005] simultaneously with local-

scale measurements of snowmelt/evaporation and energy balance within and outside the urban area.

#### 3.3.4. Impacts of Elevated $\text{H}_2\text{O}_v$ on the Urban Heat Island

Radiative forcing by anthropogenic GHG emissions is often considered in terms of global temperature increase. But the question remains as to whether the combined effects of elevated  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}_v$  can impact the intensity of the daytime UHI. On average, the air advected out of the D.C.-Balt area was elevated in  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}_v$ , by 4 ppm, 26 ppb, and 0.43 mmol  $\text{mol}^{-1}$ , respectively, on days when an urban  $\text{H}_2\text{O}_v$  excess signal was observed. Past studies have considered the impact of elevated urban GHG mole fractions on UHI intensity [Oke *et al.*, 1991; Holmer and Eliasson, 1999; McCarthy *et al.*, 2010]. For some of these studies,  $\text{H}_2\text{O}_v$  [Holmer and Eliasson, 1999] or  $\text{CO}_2$  [McCarthy *et al.*, 2010] were considered individually, or the focus was on simulating the nighttime UHI [Oke *et al.*, 1991; Holmer and Eliasson, 1999].

The impact of enhanced urban GHG mole fractions on UHI intensity was assessed through idealized experiments using the Rapid Radiative Transfer Model (RRTM; methods discussed in the SI). Our calculations from RRTM show that on all five days the urban enhancement in  $\text{CO}_2$  and  $\text{CH}_4$  mole fractions had a negligible impact on the longwave radiation budget. McCarthy *et al.* [2010] show that the UHI intensity of megacities are positively influenced in the hypothetical scenario of increasing the global atmospheric  $\text{CO}_2$  mole fraction to 645 ppm. Their analysis, however, is extreme in comparison to our simulation of the relative impact, which used the average observed urban enhancement in  $\text{CO}_2$  mole fraction, 4 ppm, for a total of 412 ppm  $\text{CO}_2$  well-mixed throughout the D.C.-Balt boundary layer. Enhanced  $\text{H}_2\text{O}_v$  had a larger, but still minimal, impact on the longwave radiation budget than  $\text{CO}_2$  and  $\text{CH}_4$ . Relative to the control scenario, elevated  $\text{H}_2\text{O}_v$  mole fractions produced a cooling of roughly  $-0.1^\circ\text{C day}^{-1}$  at the top of the boundary layer, and a comparable warming of  $0.1^\circ\text{C day}^{-1}$  at the surface (Figure S8). These values are small, but could contribute to the average afternoon UHI of  $\sim 1.5^\circ\text{C}$  observed in Washington, D.C. in winter by 6-7% at the surface [Hicks *et al.*, 2010]. Absorption of shortwave radiation (warming) by  $\text{H}_2\text{O}_v$  during the daytime is less in magnitude than longwave cooling, thus producing a net cooling within the boundary layer during the day that is less than  $-0.1^\circ\text{C day}^{-1}$ . Holmer and Eliasson [1999] also report competing impacts from elevated urban humidity on UHI intensity, which result in a net cooling effect. The small GHG-induced

637 radiative impacts in the urban plume suggested by these calculations are consistent with results  
638 from previous studies [*Oke et al.*, 1991; *Holmer and Eliasson*, 1999].

639



#### 4. Conclusions

Our wintertime airborne case studies around D.C.-Balt and Indianapolis reveal instances of significant urban emissions of  $\text{H}_2\text{O}_v$  that result in  $\text{H}_2\text{O}_v$  mole fractions downwind of the urban area to be in excess of rural  $\text{H}_2\text{O}_v$  mole fractions. On flight days when an elevated  $\text{H}_2\text{O}_v$  signal was observed, the emission rate of excess urban  $\text{H}_2\text{O}_v$  ranged between  $1.6 (\pm 0.66) \times 10^4 - 1.7 (\pm 0.81) \times 10^5$  and  $2.1 (\pm 1.2) \times 10^4 - 3.5 (\pm 1.4) \times 10^4 \text{ kg s}^{-1}$  for D.C.-Balt and Indianapolis, respectively. The emissions of excess urban  $\text{H}_2\text{O}_v$  contributed between 1.5-8.4% to the total flow of atmospheric boundary layer  $\text{H}_2\text{O}_v$  out of the urban areas. Our observations of urban  $\text{H}_2\text{O}_v$  excess occurred during times of the year when transpiration rates were likely very low. Furthermore, because of the low temperatures associated with winter, saturation vapor pressure is lower than in summer months, and urban  $\text{H}_2\text{O}_v$  excess signals are easier to observe relative to the noise, or natural variability in  $\text{H}_2\text{O}_v$  mole fractions.

To our knowledge this is the first study to report elevated  $\text{H}_2\text{O}_v$  mole fractions downwind of an urban area using airborne platforms during daytime, and which has shown city-wide  $\text{H}_2\text{O}_v$  excess, rather than local scale observations. Previous urban-rural humidity studies employed mobile [Chandler, 1967; Kopec, 1973; Richards, 2005] and airborne platforms [Bornstein and Tam, 1977; Sisterson and Dirks, 1978] to traverse larger rural and urban areas, but none reported elevated moisture levels downwind of cities during midday. Studies of urban-rural humidity gradients and energy balance studies typically employ meteorological and eddy covariance towers, where the locations of rural stations are purposely chosen so that they are not influenced by a nearby urban center. Urban areas are heterogeneous, and thus tower location would be very important.

A combination of sources and conditions was likely responsible for the observed urban  $\text{H}_2\text{O}_v$  signal reported here. Using  $\text{CO}_2$  emissions estimates and a combustion fuel consumption-weighted  $\text{H}_2\text{O}_v:\text{CO}_2$  ratio, it was estimated that combustion sources contributed a maximum of 9.6% to the elevated urban  $\text{H}_2\text{O}_v$  signal, and only contributed a maximum of 0.32% of the total transport of boundary layer  $\text{H}_2\text{O}_v$  through the study areas. We have shown that contributions from evaporative cooling towers when energy generation facilities are operating at maximum capacities could account for approximately 2% to 43% of the observed urban  $\text{H}_2\text{O}_v$  excess signals. A dominant source contributing to the urban  $\text{H}_2\text{O}_v$  signal could be rapid urban snowmelt

and evaporation either from increased wintertime anthropogenic heat flux and/or advection-assisted evaporation. We note that prior precipitation events do not necessarily lead to observable urban  $\text{H}_2\text{O}_v$  signals. Combining mobile city-scale  $\text{H}_2\text{O}_v$  measurements with micro- and local-scale measurements of snowmelt, evaporation, and energy fluxes at several rural and urban sites could be a next step in directly determining the relative contribution of these processes to the urban  $\text{H}_2\text{O}_v$  excess signal.

We quantified the impact of GHG radiative forcing on the intensity of the UHI using RRTM, and found that elevated urban mole fractions of  $\text{H}_2\text{O}_v$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  individually, and collectively, had small impacts on UHI intensity. At the surface, elevated urban mole fractions of  $\text{H}_2\text{O}_v$  could be responsible for 6-7% of UHI intensity. However, this surface warming is counteracted by longwave cooling at the top of the boundary layer. Atmospheric boundary layer effects caused by urban  $\text{H}_2\text{O}_v$  emissions could be significant, and include urban area-modified downwind cloud cover and weather [Mölders and Olson, 2004; Rosenfeld *et al.*, 2008; Trusilova *et al.*, 2008; Twohy *et al.*, 2009; Kourtidis *et al.*, 2015]. In addition, recent findings indicate that aerosol chemistry and optical properties could be modified in the downwind region of the urban environment [Twohy *et al.*, 2009; Carlton and Turpin, 2013; Hodas *et al.*, 2014; Guo *et al.*, 2015; Rindelaub *et al.*, 2015].

## Acknowledgments and Data

We thank Joel A. Thornton and Steven S. Brown for organizing and inviting us to take part in the WINTER campaign. We are grateful for help with the design, installation, and maintenance of the ALAR instrument package we received from Purdue University's Jonathan Amy Facility for Chemical Instrumentation. We thank Daniel P. Sarmiento for reading and suggesting improvements to this manuscript. We acknowledge support for this research from James Whetstone and the National Institute of Standards and Technology (NIST), for which we are grateful. We also thank three anonymous reviewers for valuable input on this manuscript. The UMD and Purdue flight experiments and analysis were supported by NIST Award 70NANB14H333 and 70NANB14H332, respectively. The radiative transfer modeling was supported by the National Aeronautics and Space Administration's Earth Science Research Program. All airborne data collected during the WINTER campaign by the Purdue and UMD aircraft are available on the WINTER Data Archive at EOL: [http://data.eol.ucar.edu/master\\_list/?project=WINTER](http://data.eol.ucar.edu/master_list/?project=WINTER). Purdue University airborne data collected in Indianapolis as part of the INFLUX campaign are available at: <http://sites.psu.edu/influx/data/>. The authors declare no competing financial interest.

## References

- Acevedo, O. C., and D. R. Fitzjarrald (2001), The Early Evening Surface-Layer Transition: Temporal and Spatial Variability, *Journal of the Atmospheric Sciences*, 58(17), 2650-2667, doi: 10.1175/1520-0469(2001)058<2650:teeslt>2.0.co;2.
- Ackerman, B. (1987), Climatology of Chicago Area Urban-Rural Differences in Humidity, *J. Clim. Appl. Meteorol.*, 26(3), 427-430, doi: doi:10.1175/1520-0450(1987)026<0427:COCAUR>2.0.CO;2.
- Arnfield, A. J. (2003), Two decades of urban climate research: a review of turbulence, exchanges of energy and water, and the urban heat island, *Int. J. Climatol.*, 23(1), 1-26, doi: 10.1002/joc.859.
- Ao, X., C. S. B. Grimmond, Y. Chang, D. Liu, Y. Tang, P. Hu, Y. Wang, J. Zou, and J. Tan (2016), Heat, water and carbon exchanges in the tall megacity of Shanghai: challenges and results, *Int. J. Climatol.*, 36(14), 4608-4624, doi: 10.1002/joc.4657.
- Bengtsson, L., and G. Westerström (1992), Urban snowmelt and runoff in northern Sweden, *Hydrol. Sci. J.*, 37(3), 263-275, doi: 10.1080/02626669209492586.
- Berg, L., and K. J. Allwine (2006), An Analysis of Wintertime Winds in Washington, DC, edited, PNNL-15799, Pacific Northwest National Laboratory, Richland, Washington. Bergeron, O., and I. B. Strachan (2012), Wintertime radiation and energy budget along an urbanization gradient in Montreal, Canada, *Int. J. Climatol.*, 32(1), 137-152, doi: 10.1002/joc.2246.
- Bornstein, R. D., Tam, Y.-T. (1977), Anthropogenic moisture production and its effect on boundary-layer circulations over New York City, paper presented at Heisler, Gordon M.; Herrington, Lee P., eds. Proceedings of the conference on metropolitan physical environment; Gen. Tech. Rep. NE-25., Upper Darby, PA: U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station.
- Bosilovich, M. G., S. Akella, L. Coy, R. Cullather, C. Draper, R., and R. K. Gelaro, Q. Liu, A. Molod, P. Norris, et al. (2015), MERRA-2: Initial evaluation of the climate. NASA/TM-2015-104606, 43, 139.
- Brent, L. C., W. J. Thorn, M. Gupta, J. B. Leen, J. W. Stehr, H. He, H. L. Arkinson, A. Weinheimer, C. Garland, S. E. Pusede, et al. (2015), Evaluation of the use of a commercially available cavity ringdown absorption spectrometer for measuring NO<sub>2</sub> in flight, and observations over the Mid-Atlantic States, during DISCOVER-AQ, *J. Atmos. Chem.*, 72(3), 503-521, doi: 10.1007/s10874-013-9265-6.
- Bréon, F.-M. (2006), How Do Aerosols Affect Cloudiness and Climate?, *Science*, 313(5787), 623-624, doi: 10.1126/science.1131668. Cambaliza, M. O. L., P. B. Shepson, D. R. Caulton, B. H. Stirm, D. Samarov, K. R. Gurney, J. Turnbull, K. J. Davis, A. Possolo, A. Karion., et al. (2014), Assessment of uncertainties of an aircraft-based mass balance approach for quantifying urban greenhouse gas emissions, *Atmos. Chem. Phys.*, 14(17), 9029-9050, doi: 10.5194/acp-14-9029-2014.

742 Cambaliza, M. O. L., P. B. Shepson, J. Bogner, D. R. Caulton, B. H. Stirm, C. Sweeney, S. A.  
 743 Montzka, K. R. Gurney, K. Spokas, O. E. Salmon, et al. (2015), Quantification and source  
 744 apportionment of the methane emission flux from the city of Indianapolis, *Elementa*, 3(1),  
 745 000037, doi: 10.12952/journal.elementa.000037.

746 Carlton, A. G., and B. J. Turpin (2013), Particle partitioning potential of organic compounds is  
 747 highest in the Eastern US and driven by anthropogenic water, *Atmos. Chem. Phys.*, 13(20),  
 748 10203-10214, doi: 10.5194/acp-13-10203-2013.Center for International Earth Science  
 749 Information Network - CIESIN - Columbia University, International Food Policy Research  
 750 Institute - IFPRI, The World Bank, and Centro Internacional de Agricultura Tropical - CIAT  
 751 (2011), *Global Rural-Urban Mapping Project, Version 1 (GRUMPv1): Population Count Grid*,  
 752 NASA Socioeconomic Data and Applications Center (SEDAC), Palisades, NY.

753 Chandler, T. (1967), Absolute and relative humidities in towns, *Bull. Amer. Meteor. Soc.*, 48(6),  
 754 394-399.

755 Chung, E.-S., B. Soden, B. Sohn, and L. Shi (2014), Upper-tropospheric moistening in response  
 756 to anthropogenic warming, *Proc. Natl. Acad. Sci.*, 111(32), 11636-11641, doi:  
 757 10.1073/pnas.1409659111.

758 Christen, A. (2014), Atmospheric measurement techniques to quantify greenhouse gas emissions  
 759 from cities, *Urban Climate*, 10, Part 2, 241-260, doi:  
 760 <http://dx.doi.org/10.1016/j.uclim.2014.04.006>.

761 Crawford, T. L., and R. J. Dobosy (1992), A sensitive fast-response probe to measure turbulence  
 762 and heat flux from any airplane, *Bound.-Layer Meteo.*, 59(3), 257-278, doi:  
 763 10.1007/BF00119816.

764 Deosthali, V. (2000), Impact of rapid urban growth on heat and moisture islands in Pune City,  
 765 India, *Atmos. Environ.*, 34(17), 2745-2754, doi: 10.1016/S1352-2310(99)00370-2.

766 Fattouh, B. (2014), The US Shale Revolution and the Changes in LPG Trade Dynamics: A  
 767 Threat to the GCC?, edited, Oxford Energy Comment.

768 Font, A., C. S. B. Grimmond, S. Kotthaus, J. A. Morgu , C. Stockdale, E. O'Connor, M.  
 769 Priestman, and B. Barratt (2015), Daytime CO2 urban surface fluxes from airborne  
 770 measurements, eddy-covariance observations and emissions inventory in Greater London,  
 771 *Environ. Pollut.*, 196, 98-106, doi: <http://dx.doi.org/10.1016/j.envpol.2014.10.001>.

772 Garman, K., K. Hill, P. Wyss, M. Carlsen, J. Zimmerman, B. Stirm, T. Carney, R. Santini, and P.  
 773 Shepson (2006), An Airborne and Wind Tunnel Evaluation of a Wind Turbulence Measurement  
 774 System for Aircraft-Based Flux Measurements\*, *J. Atmos. Oceanic Technol.*, 23(12), 1696-  
 775 1708, doi: <http://dx.doi.org/10.1175/JTECH1940.1>.

776 Gioli, B., M. F. Carfora, V. Magliulo, M. C. Metallo, A. A. Poli, P. Toscano, and F. Miglietta  
 777 (2014), Aircraft mass budgeting to measure CO2 emissions of Rome, Italy, *Environ. Monit.*  
 778 *Assess.*, 186(4), 2053-2066, doi: 10.1007/s10661-013-3517-4.

779 Global Modeling and Assimilation Office (GMAO) (2015a), MERRA-2 tavg3\_3d\_asm\_Nv:  
780 3d,3-Hourly,Time-Averaged,Model-Level,Assimilation,Assimilated Meteorological Fields  
781 V5.12.4, version 5.12.4, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information  
782 Services Center (GES DISC), doi:10.5067/SUOQESM06LPK.

783 Global Modeling and Assimilation Office (GMAO) (2015b), MERRA-2 tavg1\_2d\_slv\_Nx: 2d,1-  
784 Hourly,Time-Averaged,Single-Level,Assimilation,Single-Level Diagnostics V5.12.4, version  
785 5.12.4, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center  
786 (GES DISC), doi:10.5067/VJAFPLI1CSIV.

787 Gorski, G., C. Strong, S. P. Good, R. Bares, J. R. Ehleringer, and G. J. Bowen (2015), Vapor  
788 hydrogen and oxygen isotopes reflect water of combustion in the urban atmosphere, *Proc. Natl.*  
789 *Acad. Sci.*, 112(11), 3247-3252, doi: 10.1073/pnas.1424728112.

790 Grimmond, C. S. B. (1992), The suburban energy balance: Methodological considerations and  
791 results for a mid-latitude west coast city under winter and spring conditions, *Int. J. Climatol.*,  
792 12(5), 481-497, doi: 10.1002/joc.3370120506.

793 Grimmond, C. S. B., M. Blackett, M. J. Best, J. Barlow, J.-J. Baik, S. E. Belcher, S. I.  
794 Bohnenstengel, I. Calmet, F. Chen, A. Dandou, et al. (2010), The International Urban Energy  
795 Balance Models Comparison Project: First Results from Phase 1, *J. Appl. Meteorol. Climatol.*,  
796 49(6), 1268-1292, doi: doi:10.1175/2010JAMC2354.1.

797 Guo, H., L. Xu, A. Bougiatioti, K. M. Cerully, S. L. Capps, J. R. Hite Jr, A. G. Carlton, S. H.  
798 Lee, M. H. Bergin, N. L. Ng, et al. (2015), Fine-particle water and pH in the southeastern United  
799 States, *Atmos. Chem. Phys.*, 15(9), 5211-5228, doi: 10.5194/acp-15-5211-2015.

800 Hage, K. (1972), Urban growth effects on low-temperature fog in Edmonton, *Bound.-Layer*  
801 *Meteo.*, 2(3), 334-347, doi: 10.1007/BF02184774.

802 Hage, K. (1975), Urban-rural humidity differences, *J. Appl. Meteorol.*, 14(7), 1277-1283, doi:  
803 [http://dx.doi.org/10.1175/1520-0450\(1975\)014<1277:URHD>2.0.CO;2](http://dx.doi.org/10.1175/1520-0450(1975)014<1277:URHD>2.0.CO;2).

804 Hall, S. J., J. Learned, B. Ruddell, K. L. Larson, J. Cavender-Bares, N. Bettez, P. M. Groffman,  
805 J. M. Grove, J. B. Heffernan, S. E. Hobbie, et al. (2016), Convergence of microclimate in  
806 residential landscapes across diverse cities in the United States, *Landscape Ecol.*, 31(1), 101-117,  
807 doi: 10.1007/s10980-015-0297-y.

808 Hane, C. E. (1978), The application of a 2-D convective cloud model to waste heat release from  
809 proposed nuclear energy centers, *Atmos. Environ.*, 12(9), 1839-1848, doi:  
810 [http://dx.doi.org/10.1016/0004-6981\(78\)90003-3](http://dx.doi.org/10.1016/0004-6981(78)90003-3).

811 He, H., K. Y. Vinnikov, C. Li, N. A. Krotkov, A. R. Jongeward, Z. Li, J. W. Stehr, J. C. Hains,  
812 and R. R. Dickerson (2016), Response of SO<sub>2</sub> and particulate air pollution to local and regional  
813 emission controls: A case study in Maryland, *Earth's Future*, 4(4), 94-109, doi:  
814 10.1002/2015ef000330.

815 He, H., C. P. Loughner, J. W. Stehr, H. L. Arkinson, L. C. Brent, M. B. Follette-Cook, M. A.  
816 Tzortziou, K. E. Pickering, A. M. Thompson, D. K. Martins, et al. (2014), An elevated reservoir  
817 of air pollutants over the Mid-Atlantic States during the 2011 DISCOVER-AQ campaign:  
818 Airborne measurements and numerical simulations, *Atmos. Environ.*, 85, 18-30, doi:  
819 <http://dx.doi.org/10.1016/j.atmosenv.2013.11.039>.

820 Heimbürger, A. M., R. M. Harvey, P. B. Shepson, B. H. Stirm, C. Gore, J. Turnbull, M. O.  
821 Cambaliza, O. E. Salmon, A.-E. M. Kerlo, and T. N. Lavoie (2017), Assessing the optimized  
822 precision of the aircraft mass balance method for measurement of urban greenhouse gas emission  
823 rates through averaging, *Elem Sci Anth*, 5, doi: <http://doi.org/10.1525/elementa.134>. Hicks, B. B.,  
824 W. J. Callahan, and M. A. Hoekzema (2010), On the Heat Islands of Washington, DC, and New  
825 York City, NY, *Bound.-Layer Meteorol.*, 135(2), 291-300, doi: 10.1007/s10546-010-9468-1.

826 Ho, C., and C. Valeo (2005), Observations of urban snow properties in Calgary, Canada, *Hydrol.*  
827 *Processes*, 19(2), 459-473, doi: 10.1002/hyp.5544.

828 Hodas, N., A. P. Sullivan, K. Skog, F. N. Keutsch, J. L. Collett Jr, S. Decesari, M. C. Facchini,  
829 A. G. Carlton, A. Laaksonen, and B. J. Turpin (2014), Aerosol liquid water driven by  
830 anthropogenic nitrate: Implications for lifetimes of water-soluble organic gases and potential for  
831 secondary organic aerosol formation, *Environ. Sci. Technol.*, 48(19), 11127-11136, doi:  
832 10.1021/es5025096.

833 Holmer, B., and I. Eliasson (1999), Urban-rural vapour pressure differences and their role in the  
834 development of urban heat islands, *Int. J. Climatol.*, 19(9), 989-1009, doi: 10.1002/(sici)1097-  
835 0088(199907)19:9<989::aid-joc410>3.0.co;2-1.

836 Järvi, L., C. S. B. Grimmond, M. Taka, A. Nordbo, H. Setälä, and I. B. Strachan (2014),  
837 Development of the Surface Urban Energy and Water Balance Scheme (SUEWS) for cold  
838 climate cities, *Geosci. Model Dev.*, 7(4), 1691-1711, doi: 10.5194/gmd-7-1691-2014.

839 Kalanda, B., T. R. Oke, and D. Spittlehouse (1980), Suburban energy balance estimates for  
840 Vancouver, BC, using the Bowen ratio-energy balance approach, *J. Appl. Meteorol.*, 19(7), 791-  
841 802, doi: 10.1175/1520-0450(1980)019<0791:SEBEFV>2.0.CO;2.

842 Kalthoff, N., U. Corsmeier, K. Schmidt, C. Kottmeier, F. Fiedler, M. Habram, and F. Slemr  
843 (2002), Emissions of the city of Augsburg determined using the mass balance method, *Atmos.*  
844 *Environ.*, 36, *Supplement 1*, 19-31, doi: [http://dx.doi.org/10.1016/S1352-2310\(02\)00215-7](http://dx.doi.org/10.1016/S1352-2310(02)00215-7).

845 Karion, A., C. Sweeney, G. Pétron, G. Frost, R. Michael Hardesty, J. Kofler, B. R. Miller, T.  
846 Newberger, S. Wolter, and R. Banta (2013), Methane emissions estimate from airborne  
847 measurements over a western United States natural gas field, *Geophys. Res. Lett.*, 40(16), 4393-  
848 4397, doi: 10.1002/grl.50811.

849 Karion, A., C. Sweeney, E. A. Kort, P. B. Shepson, A. Brewer, M. Cambaliza, S. A. Conley, K.  
850 Davis, A. Deng, M. Hardesty, et al. (2015), Aircraft-Based Estimate of Total Methane Emissions  
851 from the Barnett Shale Region, *Environ. Sci. Technol.*, 49(13), 8124-8131, doi:  
852 10.1021/acs.est.5b00217.

853 Karl, T., E. Apel, A. Hodzic, D. D. Riemer, D. R. Blake, and C. Wiedinmyer (2009), Emissions  
854 of volatile organic compounds inferred from airborne flux measurements over a megacity,  
855 *Atmos. Chem. Phys.*, 9(1), 271-285, doi: 10.5194/acp-9-271-2009.

856 Kopec, R. J. (1973), Daily spatial and secular variations of atmospheric humidity in a small city,  
857 *J. Appl. Meteorol.*, 12(4), 639-648, doi: 10.1175/1520-  
858 0450(1973)012<0639:DSASVO>2.0.CO;2.

859 Kourtidis, K., S. Stathopoulos, A. K. Georgoulas, G. Alexandri, and S. Rapsomanikis (2015), A  
860 study of the impact of synoptic weather conditions and water vapor on aerosol–cloud  
861 relationships over major urban clusters of China, *Atmos. Chem. Phys.*, 15(19), 10955-10964,  
862 doi: 10.5194/acp-15-10955-2015.

863 Kreidenweis, S. M., K. Koehler, P. J. DeMott, A. J. Prenni, C. Carrico, and B. Ervens (2005),  
864 Water activity and activation diameters from hygroscopicity data - Part I: Theory and application  
865 to inorganic salts, *Atmos. Chem. Phys.*, 5(5), 1357-1370, doi: 10.5194/acp-5-1357-2005.

866 Kuttler, W., S. Weber, J. Schonnefeld, and A. Hesselschwerdt (2007), Urban/rural atmospheric  
867 water vapour pressure differences and urban moisture excess in Krefeld, Germany, *Int. J.*  
868 *Climatol.*, 27(14), 2005-2015, doi: 10.1002/joc.1558.

869 Lauvaux, T., N. L. Miles, A. Deng, S. J. Richardson, M. O. Cambaliza, K. J. Davis, B. Gaudet,  
870 K. R. Gurney, J. Huang, D. O'Keefe, et al. (2016), High-resolution atmospheric inversion of  
871 urban CO<sub>2</sub> emissions during the dormant season of the Indianapolis Flux Experiment  
872 (INFLUX), *J. Geophys. Res.: Atmos.*, 121(10), 5213-5236, doi: 10.1002/2015jd024473.

873 Lavoie, T. N., P. B. Shepson, M. O. Cambaliza, B. H. Stirm, A. Karion, C. Sweeney, T. I.  
874 Yacovitch, S. C. Herndon, X. Lan, and D. Lyon (2015), Aircraft-based measurements of point  
875 source methane emissions in the Barnett Shale basin, *Environ. Sci. Technol.*, 49(13), 7904-7913,  
876 doi: 10.1021/acs.est.5b00410.

877 Lemonsu, A., S. Bélair, J. Mailhot, M. Benjamin, G. Morneau, B. Harvey, F. Chagnon, M. Jean,  
878 and J. Voogt (2008), Overview and First Results of the Montreal Urban Snow Experiment 2005,  
879 *J. Appl. Meteorol. Climatol.*, 47(1), 59-75, doi: 10.1175/2007jamc1639.1.

880 Leroyer, S., J. Mailhot, S. Bélair, A. Lemonsu, and I. B. Strachan (2010), Modeling the Surface  
881 Energy Budget during the Thawing Period of the 2006 Montreal Urban Snow Experiment, *J.*  
882 *Appl. Meteorol. Climatol.*, 49(1), 68-84, doi: 10.1175/2009jamc2153.1.

883 Liu, W., H. You, and J. Dou (2009), Urban-rural humidity and temperature differences in the  
884 Beijing area, *Theor. Appl. Climatol.*, 96(3), 201-207, doi: 10.1007/s00704-008-0024-6.

885 Lothon, M., F. Lohou, D. Pino, F. Couvreux, E. R. Pardyjak, J. Reuder, J. Vilà-Guerau de  
886 Arellano, P. Durand, O. Hartogensis, D. Legain, et al. (2014), The BLLAST field experiment:  
887 Boundary-Layer Late Afternoon and Sunset Turbulence, *Atmos. Chem. Phys.*, 14(20), 10931-  
888 10960, doi: 10.5194/acp-14-10931-2014.



889 Mays, K. L., P. B. Shepson, B. H. Stirm, A. Karion, C. Sweeney, and K. R. Gurney (2009),  
890 Aircraft-based measurements of the carbon footprint of Indianapolis, *Environ. Sci. Technol.*,  
891 43(20), 7816-7823, doi: 10.1021/es901326b.

892 McCarthy, M. P., M. J. Best, and R. A. Betts (2010), Climate change in cities due to global  
893 warming and urban effects, *Geophys. Res. Lett.*, 37, doi: 10.1029/2010gl042845.

894 McKain, K., A. Down, S. M. Raciti, J. Budney, L. R. Hutyra, C. Floerchinger, S. C. Herndon, T.  
895 Nehrkorn, M. S. Zahniser, and R. B. Jackson (2015), Methane emissions from natural gas  
896 infrastructure and use in the urban region of Boston, Massachusetts, *Proc. Natl. Acad. Sci.*,  
897 112(7), 1941-1946, doi: 10.1073/pnas.1416261112.

898 Meroney, R. N. (2006), CFD prediction of cooling tower drift, *Journal of Wind Engineering and*  
899 *Industrial Aerodynamics*, 94(6), 463-490, doi: <http://dx.doi.org/10.1016/j.jweia.2006.01.015>.

900 Mlawer, E. J., S. J. Taubman, P. D. Brown, M. J. Iacono, and S. A. Clough (1997), Radiative  
901 transfer for inhomogeneous atmospheres: RRTM, a validated correlated-k model for the  
902 longwave, *J. Geophys. Res.: Atmos.*, 102(D14), 16663-16682, doi: 10.1029/97JD00237.

903 Mölders, N., and M. A. Olson (2004), Impact of Urban Effects on Precipitation in High  
904 Latitudes, *Journal of Hydrometeorology*, 5(3), 409-429, doi: 10.1175/1525-  
905 7541(2004)005<0409:ioueop>2.0.co;2.

906 Moore, J., and A. D. Jacobson (2015), Seasonally varying contributions to urban CO<sub>2</sub> in the  
907 Chicago, Illinois, USA region: Insights from a high-resolution CO<sub>2</sub> concentration and  $\delta^{13}\text{C}$   
908 record, *Elementa*, 3(1), 000052, doi: 10.12952/journal.elementa.000052.

909 Moriwaki, R., and M. Kanda (2004), Seasonal and diurnal fluxes of radiation, heat, water vapor,  
910 and carbon dioxide over a suburban area, *J. Appl. Meteorol.*, 43(11), 1700-1710, doi:  
911 10.1175/JAM2153.1.

912 Moriwaki, R., M. Kanda, H. Senoo, A. Hagishima, and T. Kinouchi (2008), Anthropogenic  
913 water vapor emissions in Tokyo, *Water Resour. Res.*, 44(11), doi: 10.1029/2007WR006624.

914 National Weather Service (2016), Indianapolis and Washington, D.C.-Baltimore Climatological  
915 Information. November 2012 to March 2015. [www.weather.gov](http://www.weather.gov). National Oceanic and  
916 Atmospheric Administration and National Weather Service. [Updated daily.]

917 Neumann, N., and P. Marsh (1998), Local advection of sensible heat in the snowmelt landscape  
918 of Arctic tundra, *Hydrol. Processes*, 12(10-11), 1547-1560, doi: 10.1002/(SICI)1099-  
919 1085(199808/09)12:10/11<1547::AID-HYP680>3.0.CO;2-Z.

920 Nguyen, T. K. V., S. L. Capps, and A. G. Carlton (2015), Decreasing Aerosol Water Is  
921 Consistent with OC Trends in the Southeast US, *Environ. Sci. Technol.*, 49(13), 7843-7850, doi:  
922 10.1021/acs.est.5b00828.

923 Oke, T. (1979), Advectively-assisted evapotranspiration from irrigated urban vegetation, *Bound.-*  
924 *Layer Meteo.*, 17(2), 167-173, doi: 10.1007/BF00117976.

925 Oke, T., and J. McCaughey (1983), Suburban-rural energy balance comparisons for Vancouver,  
926 BC: an extreme case?, *Bound.-Layer Meteo.*, 26(4), 337-354, doi: 10.1007/BF00119532.

927 Oke, T., G. Zeuner, and E. Jauregui (1992), The surface energy balance in Mexico City, *Atmos.*  
928 *Environ.*, 26(4), 433-444, doi: 10.1016/0957-1272(92)90050-3.

929 Oke, T., G. Johnson, D. Steyn, and I. Watson (1991), Simulation of surface urban heat islands  
930 under 'ideal' conditions at night part 2: diagnosis of causation, *Bound.-Layer Meteo.*, 56(4), 339-  
931 358, doi: 10.1007/BF00119211.

932 Offerle, B., C. S. B. Grimmond, K. Fortuniak, K. Kłysik, and T. R. Oke (2006), Temporal  
933 variations in heat fluxes over a central European city centre, *Theor. Appl. Climatol.*, 84(1), 103-  
934 115, doi: 10.1007/s00704-005-0148-x.

935 O'Shea, S. J., G. Allen, Z. L. Fleming, S. J. B. Bauguitte, C. J. Percival, M. W. Gallagher, J. Lee,  
936 C. Helfter, and E. Nemitz (2014), Area fluxes of carbon dioxide, methane, and carbon monoxide  
937 derived from airborne measurements around Greater London: A case study during summer 2012,  
938 *J. Geophys. Res.: Atmos.*, 119(8), 4940-4952, doi: 10.1002/2013jd021269.

939 Orville, H. D., P. A. Eckhoff, J. E. Peak, J. H. Hirsch, and F. J. Kopp (1981), Numerical  
940 simulation of the effects of cooling tower complexes on clouds and severe storms, *Atmos.*  
941 *Environ.*, 15(5), 823-836, doi: [http://dx.doi.org/10.1016/0004-6981\(81\)90287-0](http://dx.doi.org/10.1016/0004-6981(81)90287-0).

942 Pétron, G., A. Karion, C. Sweeney, B. R. Miller, S. A. Montzka, G. J. Frost, M. Trainer, P. Tans,  
943 A. Andrews, and J. Kofler (2014), A new look at methane and nonmethane hydrocarbon  
944 emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin, *J.*  
945 *Geophys. Res.: Atmos.*, 119(11), 6836-6852, doi: 10.1002/2013JD021272.

946 Ramamurthy, P., E. Bou-Zeid, J. A. Smith, Z. Wang, M. L. Baeck, N. Z. Saliendra, J. L. Hom,  
947 and C. Welty (2014), Influence of Subfacet Heterogeneity and Material Properties on the Urban  
948 Surface Energy Budget, *J. Appl. Meteorol. Climatol.*, 53(9), 2114-2129, doi: 10.1175/jamc-d-13-  
949 0286.1.

950 Richards, K. (2005), Urban and rural dewfall, surface moisture, and associated canopy-level air  
951 temperature and humidity measurements for Vancouver, Canada, *Bound.-Layer Meteo.*, 114(1),  
952 143-163, doi: 10.1007/s10546-004-8947-7.

953 Rind, D., E. W. Chiou, W. Chu, J. Larsen, S. Oltmans, J. Lerner, M. P. McCormick, and L.  
954 McMaster (1991), Positive water vapour feedback in climate models confirmed by satellite data,  
955 *Nature*, 349(6309), 500-503, doi: 10.1038/349500a0.

956 Rindelaub, J. D., K. M. McAvey, and P. B. Shepson (2015), The photochemical production of  
957 organic nitrates from  $\alpha$ -pinene and loss via acid-dependent particle phase hydrolysis, *Atmos.*  
958 *Environ.*, 100, 193-201, doi: 10.1016/j.atmosenv.2014.11.010.

959 Rosenfeld, D., U. Lohmann, G. B. Raga, C. D. O'Dowd, M. Kulmala, S. Fuzzi, A. Reissell, and  
960 M. O. Andreae (2008), Flood or Drought: How Do Aerosols Affect Precipitation?, *Science*,  
961 321(5894), 1309-1313, doi: 10.1126/science.1160606.

962 Ruiz, J., A. S. Kaiser, M. Ballesta, A. Gil, and M. Lucas (2013), Experimental measurement of  
 963 cooling tower emissions using image processing of sensitive papers, *Atmos. Environ.*, 69, 170-  
 964 181, doi: <http://dx.doi.org/10.1016/j.atmosenv.2012.12.014>.

965 Sailor, D. J. (2011), A review of methods for estimating anthropogenic heat and moisture  
 966 emissions in the urban environment, *Int. J. Climatol.*, 31(2), 189-199, doi: 10.1002/joc.2106.

967 Sisterson, D. L., and R. A. Dirks (1978), Structure of the daytime urban moisture field, *Atmos.*  
 968 *Environ.*, 12(10), 1943-1949, doi: 10.1016/0004-6981(78)90129-4.

969 Solomon, S., K. H. Rosenlof, R. W. Portmann, J. S. Daniel, S. M. Davis, T. J. Sanford, and G.-K.  
 970 Plattner (2010), Contributions of stratospheric water vapor to decadal changes in the rate of  
 971 global warming, *Science*, 327(5970), 1219-1223, doi: 10.1126/science.1182488.

972 Stockham, J. (1971), Cooling Tower Study, Contract CPA 22-69-122 Rep. IITRI Project C6187,  
 973 IIT Research Institute, Chicago, IL.

974 Stull, R. B. (1988), An introduction to boundary layer meteorology, Springer Science & Business  
 975 Media.

976 Trainer, M., B. Ridley, M. Buhr, G. Kok, J. Walega, G. Hübler, D. Parrish, and F. Fehsenfeld  
 977 (1995), Regional ozone and urban plumes in the southeastern United States: Birmingham, a case  
 978 study, *J. Geophys. Res.: Atmos.*, 100(D9), 18823-18834, doi: 10.1029/95JD01641.

979 Trousdell, J. F., S. A. Conley, A. Post, and I. C. Faloona (2016), Observing entrainment mixing,  
 980 photochemical ozone production, and regional methane emissions by aircraft using a simple  
 981 mixed-layer framework, *Atmos. Chem. Phys.*, 16(24), 15433-15450, doi: 10.5194/acp-16-15433-  
 982 2016.

983 Trusilova, K., M. Jung, G. Churkina, U. Karstens, M. Heimann, and M. Claussen (2008),  
 984 Urbanization Impacts on the Climate in Europe: Numerical Experiments by the PSU-NCAR  
 985 Mesoscale Model (MM5), *J. Appl. Meteorol. Climatol.*, 47(5), 1442-1455, doi:  
 986 10.1175/2007jamc1624.1.

987 Twohy, C. H., J. A. Coakley, and W. R. Tahnk (2009), Effect of changes in relative humidity on  
 988 aerosol scattering near clouds, *J. Geophys. Res.: Atmos.*, 114(D5), doi: 10.1029/2008JD010991.

989 United Nations (UN) Human Settlements Programme (2011), Cities and Climate Change: Global  
 990 Report on Human Settlement 2011,  
 991 [http://mirror.unhabitat.org/downloads/docs/E\\_Hot\\_Cities.pdf](http://mirror.unhabitat.org/downloads/docs/E_Hot_Cities.pdf); UN, Nairobi, Kenya.

992 U.S. Census Bureau, Population Division (2010), CBSA Report Chapter 3 Data, U.S. Census  
 993 Bureau, Washington, D.C.

994 U.S. Census Bureau, Population Division (2016), Annual Estimates of the Resident Population  
 995 April 1, 2010 to July 1, 2015,  
 996 <http://factfinder.census.gov/faces/tableservices/jsf/pages/productview.xhtml?src=bkmk>, U.S.  
 997 Census Bureau, Washington, D.C.

998 U.S. Energy Information Administration (EIA) (2015), Monthly Energy Review; February to  
 999 March 2015, DOE/EIA-0484, <http://www.eia.gov/electricity/data/browser/>, U.S. EIA, Off. Of  
 1000 Energy Analysis, U.S. Dep. of Energy, Washington, D. C.

1001 U.S. Energy Information Administration (EIA) (2016a), State Profile and Energy Estimates,  
 1002 <http://www.eia.gov/state/>, U.S. EIA, Off. Of Energy Analysis, U.S. Dep. of Energy, Washington,  
 1003 D. C.

1004 U.S. Energy Information Administration (EIA) (2016b), Form EIA-860, 2015ER\*,  
 1005 <https://www.eia.gov/electricity/data/eia860/>, U.S. EIA, Off. Of Energy Analysis, U.S. Dep. of  
 1006 Energy, Washington, D. C.

1007 U.S. Environmental Protection Agency (EPA) (1998), Compilation of Air Pollutant Emission  
 1008 Factors, AP 42, Fifth Edition, Volume I, Chapter 1.4 Natural Gas Combustion,  
 1009 <http://www3.epa.gov/ttnchie1/ap42/ch01/final/c01s04.pdf> , EPA, Washington, D.C.

1010 U.S. Environmental Protection Agency (EPA) (2015), Inventory of U.S. Greenhouse Gas  
 1011 Emissions and Sinks: 1990-2013, [https://www.epa.gov/ghgemissions/sources-greenhouse-gas-](https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions)  
 1012 [emissions](https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions), EPA, Washington, D.C.

1013 Vaughan, A. R., J. D. Lee, P. K. Misztal, S. Metzger, M. D. Shaw, A. C. Lewis, R. M. Purvis, D.  
 1014 C. Carslaw, A. H. Goldstein, C. N. Hewitt, et al. (2016), Spatially resolved flux measurements of  
 1015 NO<sub>x</sub> from London suggest significantly higher emissions than predicted by inventories, *Faraday*  
 1016 *Discuss.*, 189(0), 455-472, doi: 10.1039/c5fd00170f.

1017 Ward, H. C., J. G. Evans, and C. S. B. Grimmond (2013), Multi-season eddy covariance  
 1018 observations of energy, water and carbon fluxes over a suburban area in Swindon, UK, *Atmos.*  
 1019 *Chem. Phys.*, 13(9), 4645-4666, doi: 10.5194/acp-13-4645-2013.

1020 Weston, K. C. (2000), Energy conversion—the ebook, University of Tulsa.

1021 Willett, K. M., N. P. Gillett, P. D. Jones, and P. W. Thorne (2007), Attribution of observed  
 1022 surface humidity changes to human influence, *Nature*, 449(7163), 710-712, doi:  
 1023 [http://www.nature.com/nature/journal/v449/n7163/supinfo/nature06207\\_S1.html](http://www.nature.com/nature/journal/v449/n7163/supinfo/nature06207_S1.html).

1024 World Health Organization (WHO) (2016), Global Health Observatory (GHO) data,  
 1025 [http://www.who.int/gho/urban\\_health/en/](http://www.who.int/gho/urban_health/en/), WHO, Geneva, Switzerland.

## Tables

Flight date	Precipitation amount in week prior to flight	Max enhancement in urban $\text{H}_2\text{O}_v$ mole fraction relative to background [ $\text{mmol mol}^{-1}$ ]	$\text{ER}_{\text{Urban}} (\pm 1\sigma)$ [ $\text{kg H}_2\text{O}_v \text{ s}^{-1}$ ]	$\text{ER}_{\text{Urban}}/\text{ER}_{\text{Total}}$
8 Nov 2012*	4 mm	0.72	$2.1 (\pm 1.2) \times 10^4$	2.6%
25 Nov 2014*	54 mm	0.65	$3.5 (\pm 1.4) \times 10^4$	3.0%
13 Feb 2015†	3 mm	0.31	$1.6 (\pm 0.66) \times 10^4$	1.7%
20 Feb 2015†	14 mm	0.24	$6.5 (\pm 2.8) \times 10^4$	8.4%
27 Feb 2015†	25 mm	1.49	$1.7 (\pm 0.81) \times 10^5$	5.9%
9 Mar 2015†	23 mm	1.09	$3.4 (\pm 1.6) \times 10^4$	1.5%
12 Mar 2015†	23 mm	0.78	$3.6 (\pm 1.6) \times 10^4$	3.1%

**Table 1.** Urban  $\text{H}_2\text{O}_v$  emission rate ( $\text{ER}_{\text{Urban}}$ ) estimates, maximum observed urban  $\text{H}_2\text{O}_v$  enhancement, and percent contribution of urban-derived  $\text{H}_2\text{O}_v$  to the total transport of atmospheric boundary layer  $\text{H}_2\text{O}_v$  ( $\text{ER}_{\text{Total}}$ ) out of the study sites for days when an elevated urban  $\text{H}_2\text{O}_v$  signal was observed. Also included is the precipitation amount reported in the seven days prior to the flight days by the Indianapolis International Airport for Indianapolis flights, and the average values reported by Washington National and Baltimore-Washington International Airports for D.C.-Balt flights. Precipitation amounts for snow events are reported in snow water equivalent.

\* Indianapolis

† D.C.-Balt

Flight date (low/high surface temp)	$ER_{\text{Combust}}$ [kg H <sub>2</sub> O <sub>v</sub> s <sup>-1</sup> ]	$ER_{\text{Combust}} \cdot ER_{\text{Urban}}$ [%]	$ER_{\text{Combust}} \cdot ER_{\text{Total}}$ [%]	$ER_{\text{MaxCT}}$ [kg H <sub>2</sub> O <sub>v</sub> s <sup>-1</sup> ]	$ER_{\text{MaxCT}} \cdot ER_{\text{Urban}}$ [%]	$ER_{\text{MaxCT}} \cdot ER_{\text{Total}}$ [%]
8 Nov 2012* (-2.8°C/8.9°C)	$3.7 \times 10^2$	1.8%	0.046%	$6.7 \times 10^2$	3.2%	0.084%
25 Nov 2014* (-3.3°C/2.2°C)	$3.2 \times 10^2$	0.9%	0.027%	$6.7 \times 10^2$	1.9%	0.056%
13 Feb 2015† (-10.3°C/-1.9°C)	$1.5 \times 10^3$	9.6%	0.17%	$7.4 \times 10^3$	43%	0.75%
20 Feb 2015† (-16.1°C/-6.7°C)	$2.5 \times 10^3$	3.9%	0.32%	$7.4 \times 10^3$	11%	0.87%
27 Feb 2015† (-6.4°C/2.5°C)	$1.7 \times 10^3$	1.0%	0.057%	$7.4 \times 10^3$	4.4%	0.25%
9 Mar 2015† (0.8°C/16.4°C)	$6.7 \times 10^2$	2.0%	0.028%	$7.4 \times 10^3$	21%	0.31%
12 Mar 2015† (3.3°C/14.4°C)	$3.8 \times 10^2$	1.1%	0.029%	$7.4 \times 10^3$	19%	0.56%

**Table 2.** Combustion-derived H<sub>2</sub>O<sub>v</sub> emission rate ( $ER_{\text{Combust}}$ ) and maximum cooling tower emission rate ( $ER_{\text{MaxCT}}$ ) estimates for days when an urban H<sub>2</sub>O<sub>v</sub> excess signal was observed, as well as the contribution of  $ER_{\text{Combust}}$  and  $ER_{\text{MaxCT}}$  to  $ER_{\text{Urban}}$  (urban H<sub>2</sub>O<sub>v</sub> excess emission rate) and  $ER_{\text{Total}}$  (total boundary layer H<sub>2</sub>O<sub>v</sub> flow through study site). Also provided are the low and high surface temperatures for these days reported by the Indianapolis International Airport for Indianapolis flights or the Washington National and Baltimore-Washington International Airports for D.C.-Balt flights.

\* Indianapolis

† D.C.-Balt

## Figure Captions

**Figure 1.** The ALAR (a) flight path and (b) altitude time series on 27 February 2015. After takeoff from Manassas, VA, a vertical profile (VP1) was conducted, followed by an upwind transect (UW). Three downwind transects (DW1-3) were flown along identical waypoints perpendicular to the mean wind at 390 m, 680 m, and 930 m above sea level. Because the upwind and lowest downwind transects were conducted at the same altitude (b), only the downwind data along the lowest downwind transect is shown here for comparison purposes. A second vertical profile (VP2) was flown within the urban plume during the second downwind transect. Refueling took place approximately midway through the final downwind transect. Map source: Esri, USGS, NOAA, 2010 U.S. Census. Population density is distributed by the U.S. Census Bureau's Populated Places definitions.

**Figure 2.** Background  $\text{H}_2\text{O}_v$  mole fractions (cyan) are defined from air sampled along the lateral edges of the downwind transects where mole fractions are relatively constant. Observed  $\text{H}_2\text{O}_v$  mole fractions for 27 February 2015 are colored by location and altitude (in meters above sea level). Vertical dotted lines indicate the transitions between rural- and urban-influenced air.

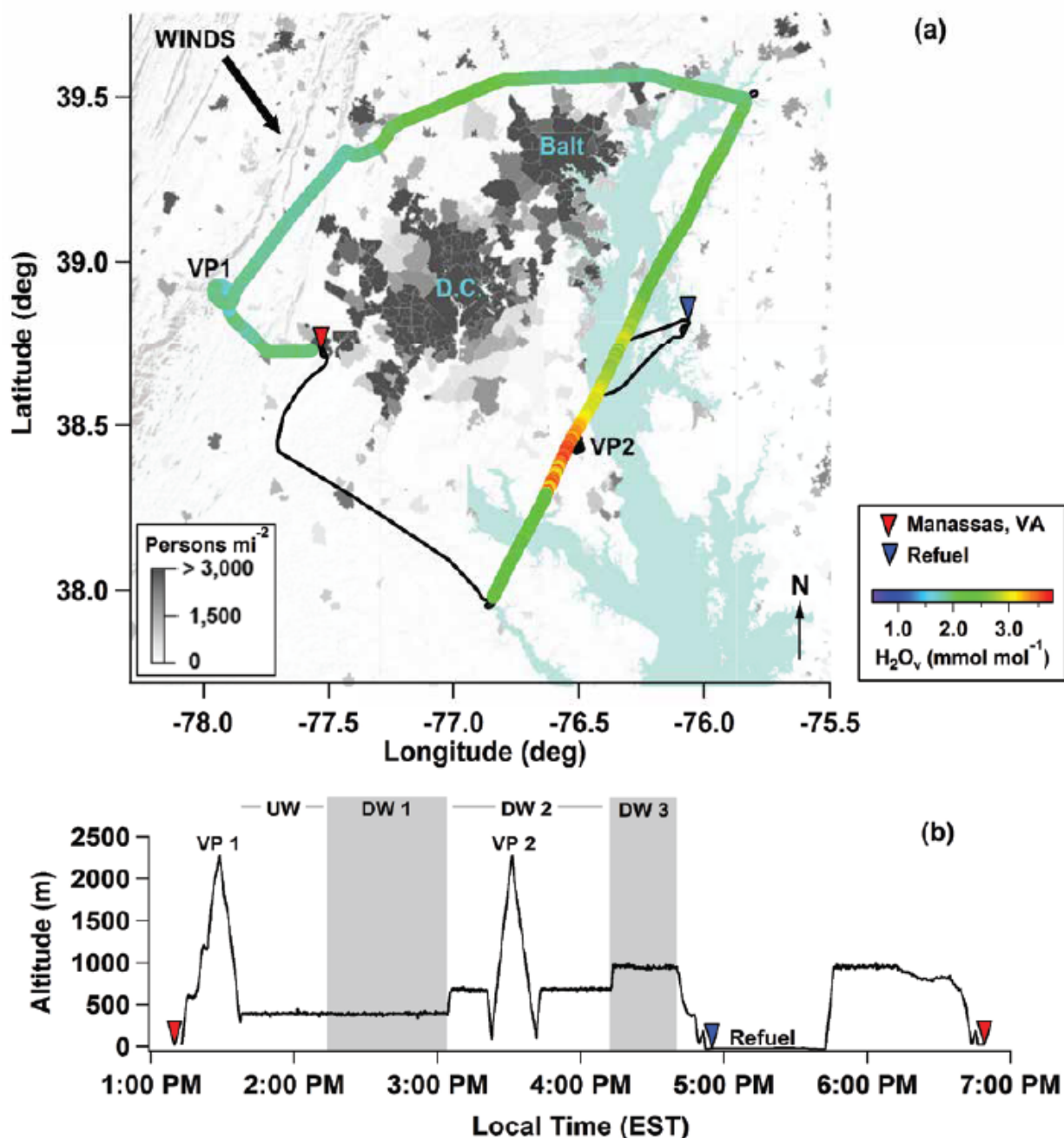
**Figure 3.** Calculated urban  $\text{H}_2\text{O}_v$  excess flux (Equation 1) at each sampling point downwind of D.C.-Balt on 27 February 2015. Boundary layer height ( $z_i$ ), defined as the altitude corresponding to the greatest change in  $d\theta/dz$ , is indicated by the horizontal dashed line. Vertical dotted lines indicate the transitions between rural- and urban-influenced air.

**Figure 4.** Urban plume profiles of (a)  $\text{H}_2\text{O}_v$ , (b)  $\text{CO}_2$ , (c)  $\text{CH}_4$ , (d)  $\text{NO}_2$ , and (e) aerosol observed downwind of D.C.-Balt on 27 February 2015. Transects are colored by location and altitude (in meters above sea level (msl)). (f) Comparison of aerosol number concentration along the upwind (390 msl in red) and lowest downwind transect (390 msl in black). (g) Comparison of the average normalized aerosol size distribution along the upwind transect and sections of the lowest downwind transect (sections identified in (f)).

**Figure 5.** Atmospheric correlation of the combustion product enhancements:  $\text{H}_2\text{O}_v$ ,  $\text{CO}_2$ , and  $\text{NO}_2$  on 27 February 2015. The data shown are background-subtracted enhancements of the atmospheric species measured within the boundary layer downwind of D.C.-Balt. The Pearson correlation coefficient ( $r$ ) for the linear relationship of  $\text{CO}_2$  and  $\text{H}_2\text{O}_v$  is  $r = 0.83$ .

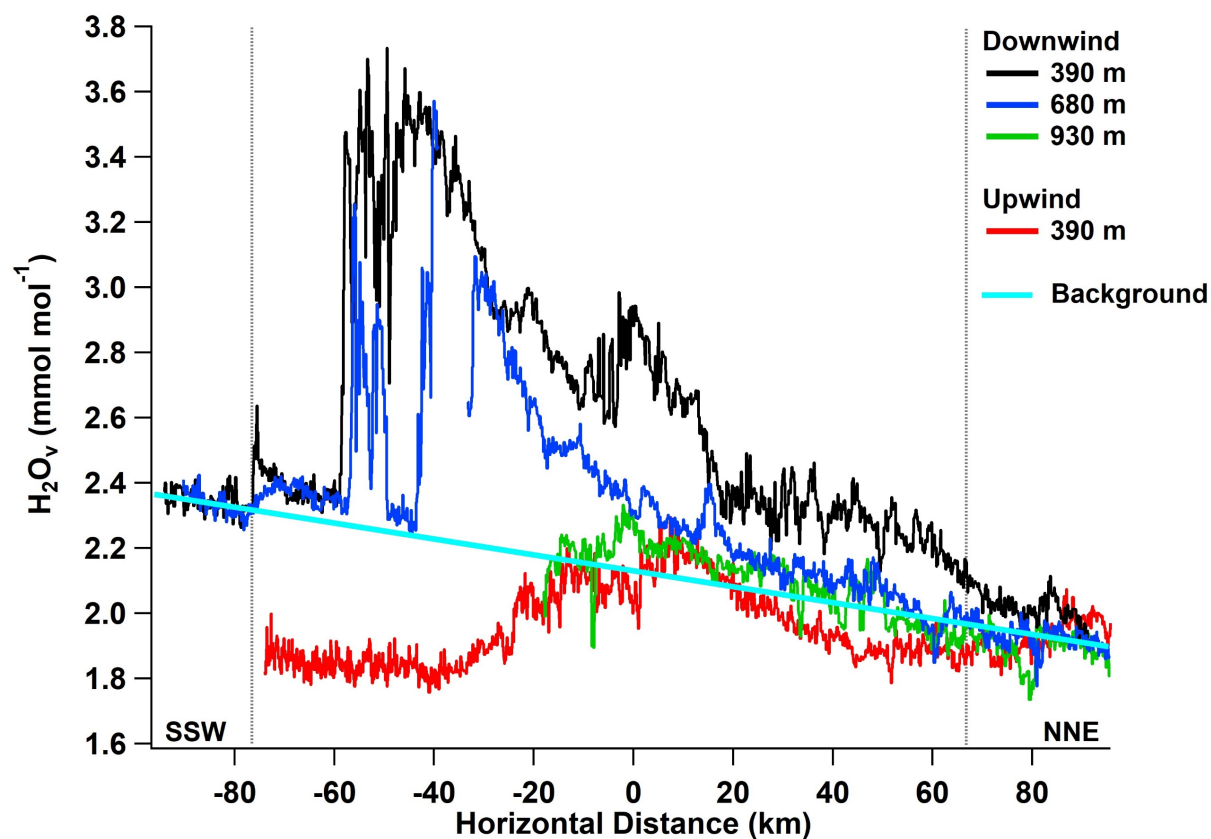
**Figure 6.** Urban plumes of (a)  $\text{H}_2\text{O}_v$ , (b)  $\text{CO}_2$ , and (c)  $\text{CH}_4$  observed downwind of Indianapolis on 8 November 2012. Urban plumes of (d)  $\text{H}_2\text{O}_v$ , (e)  $\text{CO}_2$ , and (f)  $\text{CH}_4$  observed downwind of Indianapolis on 25 November 2014. Transects are colored by altitude (meters above ground level (m agl)). Indianapolis city boundaries are indicated by the vertical dashed lines.



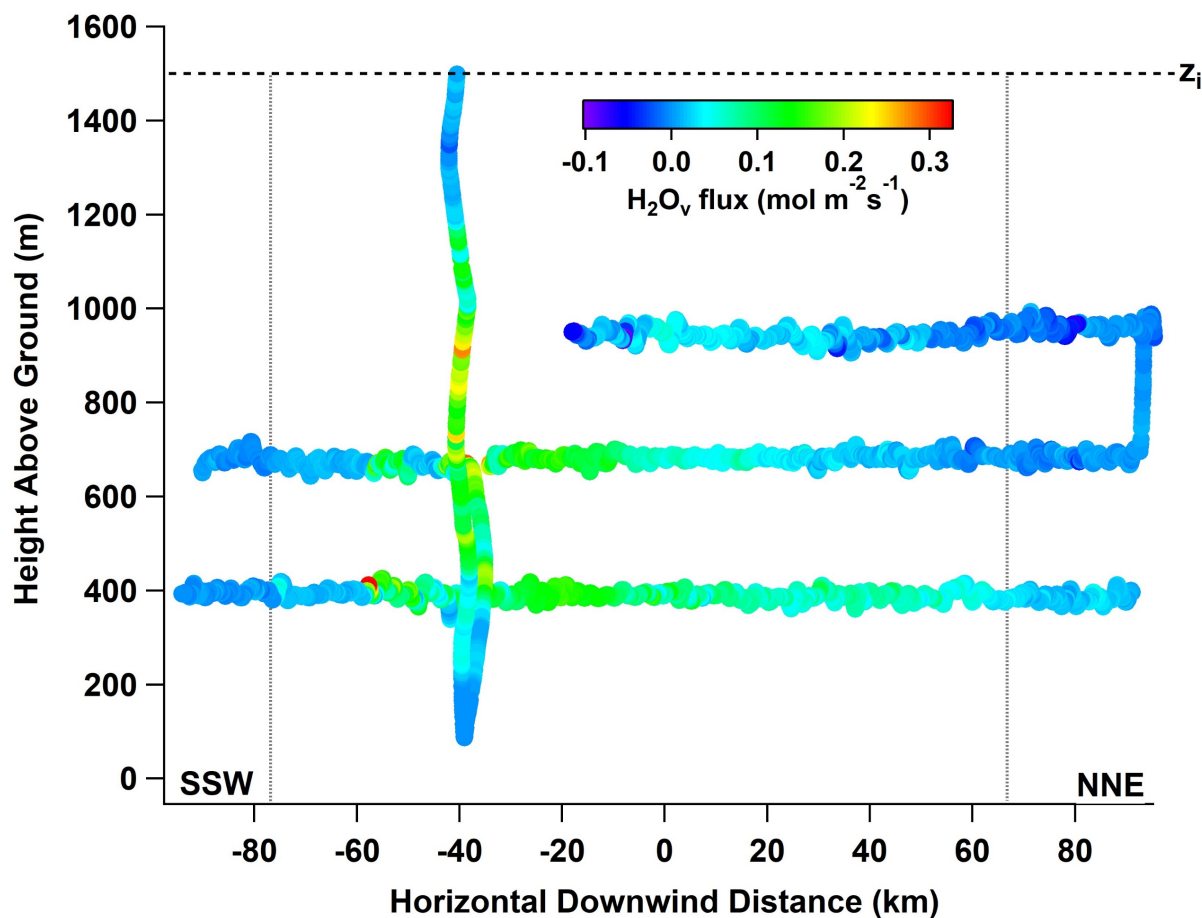


**Figure 4.** The ALAR (a) flight path and (b) altitude time series on 27 February 2015. After takeoff from Manassas, VA, a vertical profile (VP1) was conducted, followed by an upwind transect (UW). Three downwind transects (DW1-3) were flown along identical waypoints perpendicular to the mean wind at 390 m, 680 m, and 930 m above sea level. Because the upwind and lowest downwind transects were conducted at the same altitude (b), only the downwind data along the lowest downwind transect is shown here for comparison purposes. A second vertical profile (VP2) was flown within the urban plume during the second downwind transect. Refueling took place approximately midway through the final downwind transect. Map source: Esri, USGS, NOAA, 2010 U.S. Census. Population density is distributed by the U.S. Census Bureau's Populated Places definitions.

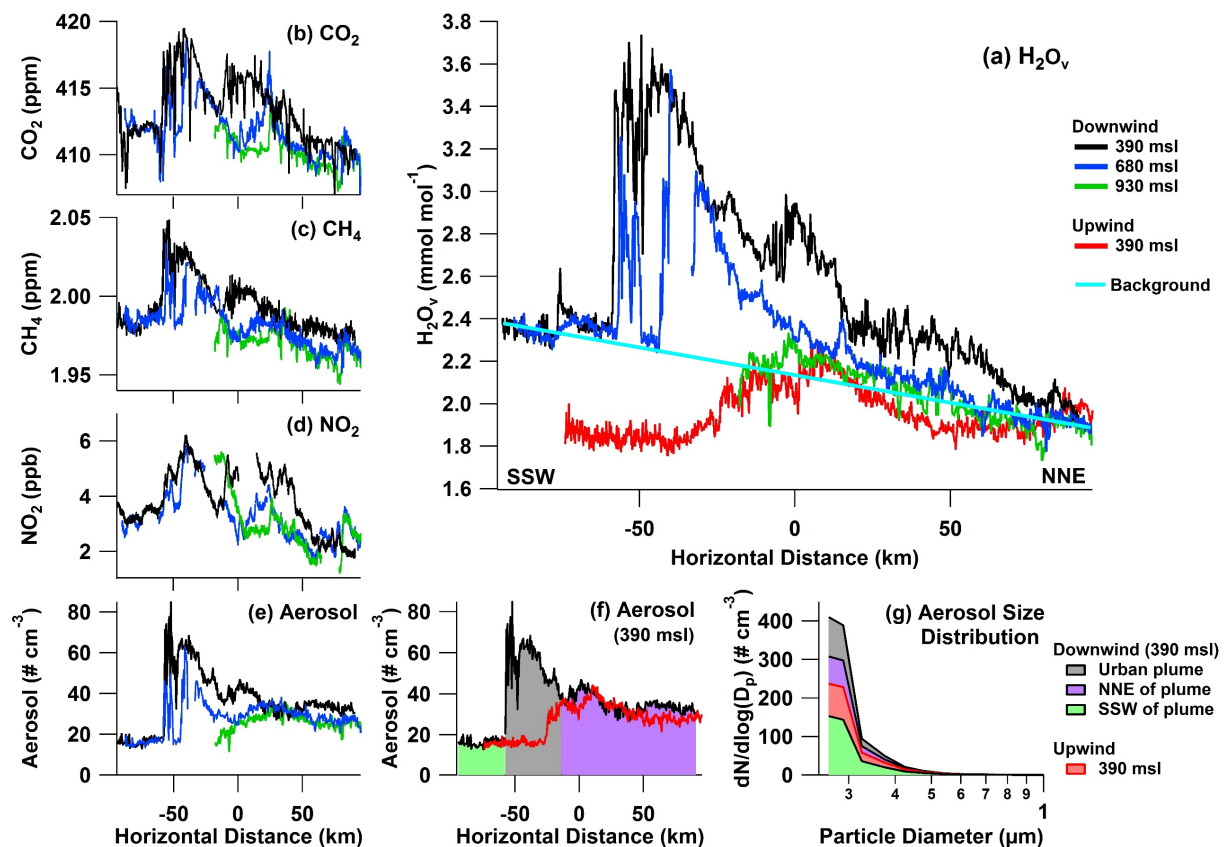




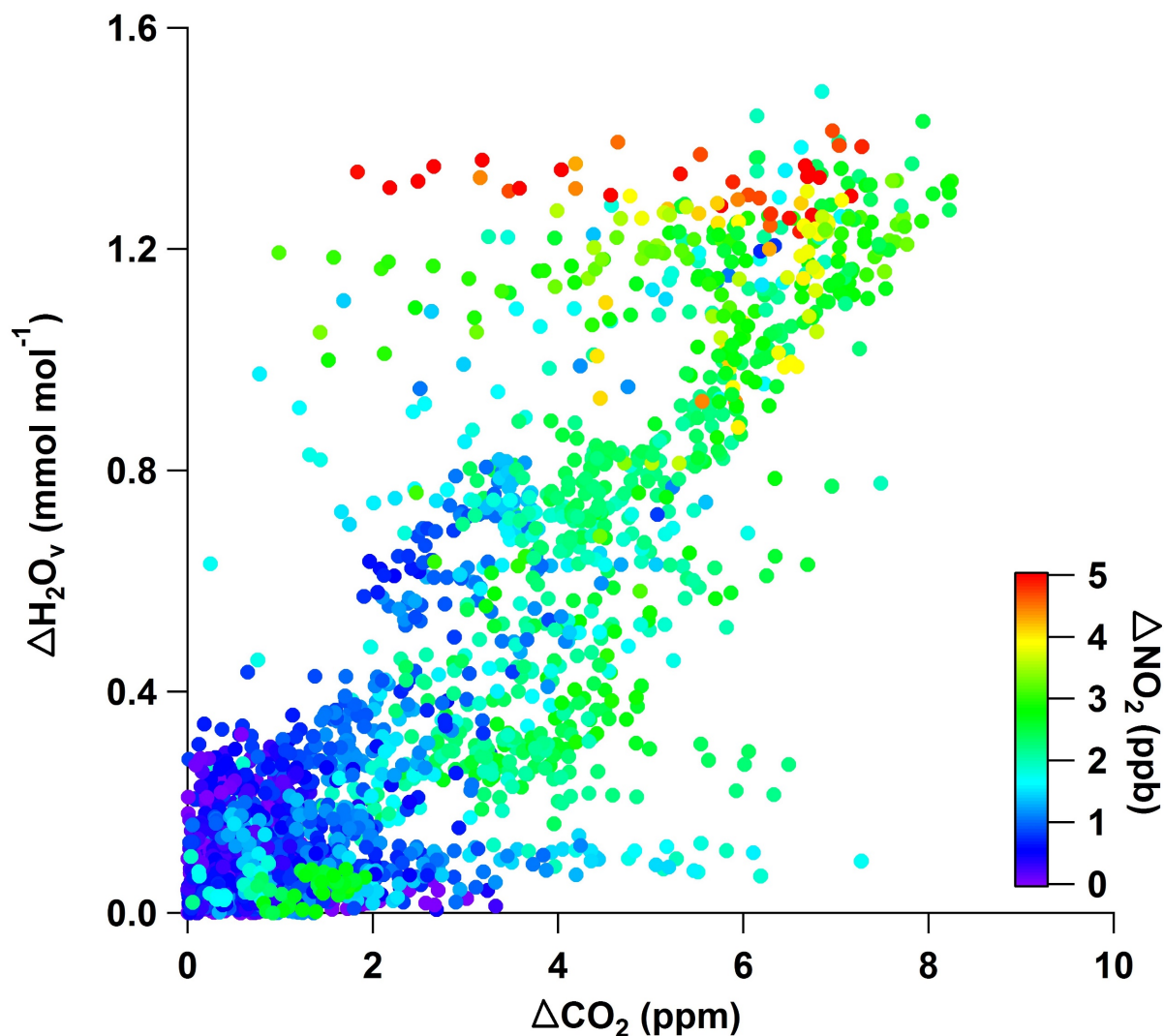
**Figure 5.** Background  $\text{H}_2\text{O}_v$  mole fractions (cyan) are defined from air sampled along the lateral edges of the downwind transects where mole fractions are relatively constant. Observed  $\text{H}_2\text{O}_v$  mole fractions for 27 February 2015 are colored by location and altitude (in meters above sea level). Vertical dotted lines indicate the transitions between rural- and urban-influenced air.



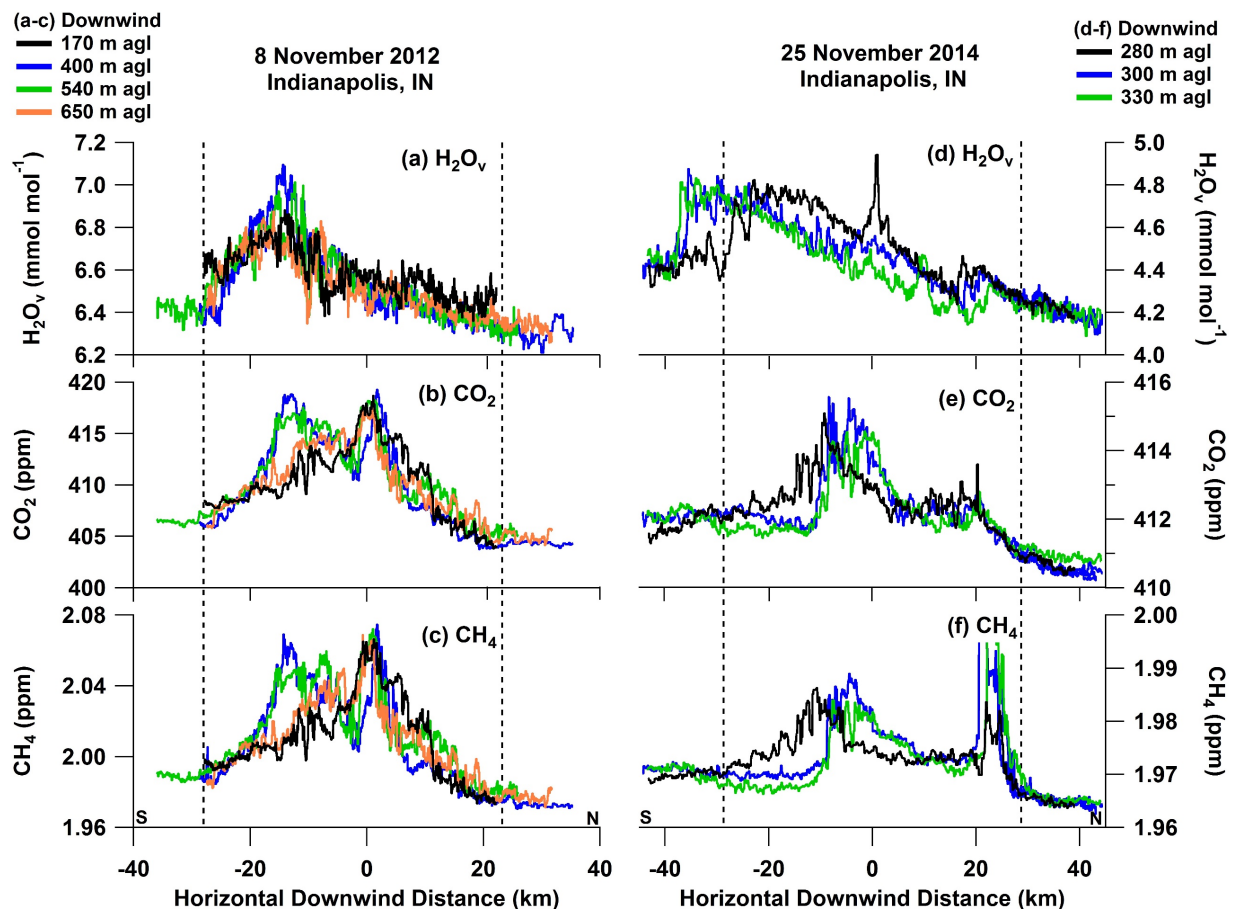
**Figure 6.** Calculated urban  $\text{H}_2\text{O}_v$  excess flux (Equation 1) at each sampling point downwind of D.C.-Balt on 27 February 2015. Boundary layer height ( $z_i$ ), defined as the altitude corresponding to the greatest change in  $d\theta/dz$ , is indicated by the horizontal dashed line. Vertical dotted lines indicate the transitions between rural- and urban-influenced air.



**Figure 4.** Urban plume profiles of (a) H<sub>2</sub>O<sub>v</sub>, (b) CO<sub>2</sub>, (c) CH<sub>4</sub>, (d) NO<sub>2</sub>, and (e) aerosol observed downwind of D.C.-Balt on 27 February 2015. Transects are colored by location and altitude (in meters above sea level (msl)). (f) Comparison of aerosol number concentration along the upwind (390 msl in red) and lowest downwind transect (390 msl in black). (g) Comparison of the average normalized aerosol size distribution along the upwind transect and sections of the lowest downwind transect (sections identified in (f)).



**Figure 5.** Atmospheric correlation of the combustion product enhancements:  $H_2O_v$ ,  $CO_2$ , and  $NO_2$  on 27 February 2015. The data shown are background-subtracted enhancements of the atmospheric species measured within the boundary layer downwind of D.C.-Balt. The Pearson correlation coefficient ( $r$ ) for the linear relationship of  $CO_2$  and  $H_2O_v$  is  $r = 0.83$ .



**Figure 6.** Urban plumes of (a)  $\text{H}_2\text{O}_v$ , (b)  $\text{CO}_2$ , and (c)  $\text{CH}_4$  observed downwind of Indianapolis on 8 November 2012. Urban plumes of (d)  $\text{H}_2\text{O}_v$ , (e)  $\text{CO}_2$ , and (f)  $\text{CH}_4$  observed downwind of Indianapolis on 25 November 2014. Transects are colored by altitude (meters above ground level (m agl)). Indianapolis city boundaries are indicated by the vertical dashed lines.